MICROCOPY RESOLUTION TEST CHART
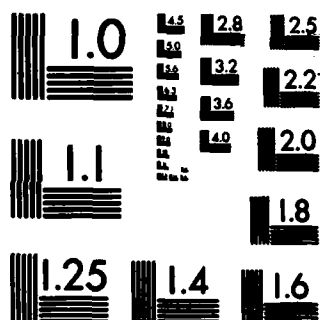NATIONAL BUREAU OF STANDARDS-1963-A

⑥

ENCAPSULATION/FIXATION (E/F) MECHANISMS

Eli Mishuck
S-CUBED, A Division of Maxwell Laboratories, Inc.
P.O. Box 1620
La Jolla, California 92038

AD-A146 177

18 June 1984

Prepared for
U.S. ARMY TOXIC AND HAZARDOUS MATERIALS AGENCY
Aberdeen Proving Ground (Edgewood Area)
Maryland 21010

DTIC
SELECTE
OCT 0 2 1984
E

DTIC FILE COPY

84 09 28 090

SECURITY CLASSIFICATION OF THIS PAGE *(When Data Entered)*

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER DRXTH-TE-CR-84298	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE *(and Subtitle)* ENCAPSULATION/FIXATION (E/F) MECHANISMS		5. TYPE OF REPORT & PERIOD COVERED Final Report 9/30/82 - 6/18/84
		6. PERFORMING ORG. REPORT NUMBER SSS-R-84-6734
7. AUTHOR(s) Mishuck, E., D.R. Taylor, R. Telles, and H. Lubowitz		8. CONTRACT OR GRANT NUMBER(s) DAAK11-82-C-0164
9. PERFORMING ORGANIZATION NAME AND ADDRESS S-CUBED 3398 Carmel Mountain Road San Diego, CA 92121		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS Title: Processes in Pollution Abatement Technology, IL1611 02AH68, Work Unit B-9
11. CONTROLLING OFFICE NAME AND ADDRESS Commander U.S. Army Toxic and Hazardous Materials Agency Aberdeen Proving Ground, MD 21010		12. REPORT DATE June 18, 1984
		13. NUMBER OF PAGES 239
14. MONITORING AGENCY NAME & ADDRESS*(If different from Controlling Office)*		15. SECURITY CLASS. *(of this report)* Unclassified
		15a. DECLASSIFICATION DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT *(of this Report)* Distribution Unlimited. Approval for Public Release June 18, 1984		
17. DISTRIBUTION STATEMENT *(of the abstract entered in Block 20, if different from Report)*		
18. SUPPLEMENTARY NOTES Basic research study conducted under the Pollution Abatement and Environmental Control Technology (PAECT) Program. Funded by USATHAMA.		
19. KEY WORDS *(Continue on reverse side if necessary and identify by block number)* Army Sludge Disposal or Sludge Treatment Army and Chemical Wastes Ammunition Plants Cementitious Fixatives Chemical Fixation Epoxy Fixatives Army and Ammunition Polysulfide Fixatives Electroplating Wastes Ion-Exchange Resin Fixatives		

20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*
The objective of this project was to examine the chemical and/or physical bonds created in the process of encapsulating/fixing AAP-type sludges. Typical sludge compositions were selected for detailed study on review of sludges generated during wastewater treatment and related operations at 22 Army facilities.

Candidate fixatives included polysilicates, amine-cured polyepoxides and polysulfides. A limited study was also conducted using ion-exchange resins

DD _{1 JAN 73} **1473**   EDITION OF 1 NOV 65 IS OBSOLETE

of the non-ionic type for sludges containing TNT and RDX; and cationic exchangers with specific chemically reactive groups for sludges containing heavy metals. The measure of effectiveness of the AAP sludge-fixative combination was EPA's EP Toxicity Test. Instrumentation characterization methods included optical microscopy, infrared spectroscopy, scanning electron microscopy, energy-dispersive X-ray analysis, and X-ray diffraction.

Polysilicates were found to fix heavy metals as a consequence of the highly alkaline-buffered media they provide. Nitrocellulose was observed to react with epoxy ingredients with the possible removal of nitrato groups. Studies with polysulfides and ion-exchange resins were encouraging, resulting in chemically fixed sludges of high contaminant density and resistance to leaching.

Accession For		
NTIS GRA&I		☒
DTIC TAB		☐
Unannounced		☐
Justification		
By		
Distribution/		
Availability Codes		
Dist	Avail and/or Special	
A-1		

EXECUTIVE SUMMARY

A literature survey of E/F materials for AAP sludges resulted in the selection of polysilicates, amine-cured epoxides and polysulfides as fixatives (binders). Two synthetic sludge candidates were formulated which contained either (a) inorganic toxicants or (b) organic toxicants. Each synthetic sludge was divided further into "wet" or aqueous solutions-suspensions and "dry" or dewatered sludges. The fixatives were selected based upon their ability to react (and form chemical and/or physical bonds) with the contaminants, their low cost and ready availability, the ease of processing, and the good physical properties anticipated. Ion-exchange resins were included later in the project (Phase IV) because these polymeric materials offered the potential for evaluating the efficacy of specific chemical functional groups in forming chemical bonds with contaminants.

Laboratory studies of heavy metal sludges treated with polysilicates indicated that the promising EP Toxicity Test results were a consequence of a highly alkaline-buffered media and that true chemical fixation probably did not occur. Instead, it was found that the alkaline Portland cement and fly ash additives normally used with polysilicates neutralized the acetic acid employed in the EP Toxicity Test, thereby preventing dissolution of the insoluble metal precipitates. These findings were supported by similar successful EP Toxicity Test results for identical cured and uncured heavy metal-polysilicate mixtures, indicating that the primary criteria to effect leaching stability did not involve incorporation of the metals into a three-dimensional (cured) network. Infrared, scanning electron microscope, energy-dispersive X-ray, and X-ray diffraction measurements of calcium polysilicate-fixed AAP sludges containing lead nitrate did not reveal the presence of new compounds or crystalline structures indicative of chemical fixation.

A computer program, GEOCHEM, was employed as a means of predicting heavy metal concentration and soluble metal behavior in mixtures of lead nitrate, sodium silicate and calcium chloride at varying pHs and ionic strengths. The results were promising and may offer a means to estimate the environmental availability of the different metal species present in soil.

Polyepoxides were used successfully to fix synthetic sludges containing up to ten (10) weight percent nitrocellulose (NC) fines (produced at Radford AAP) and up to 54 weight percent solids. Diethylenetriamine (DETA), which was used to cure the epoxide, was discovered to undergo a chemical reaction (strong exotherm) with NC. Infrared absorption measurements of mixtures of the two showed the disappearance of the two strong NC peaks at 1275 cm^{-1} and 1650 cm^{-1} and the formation of a small peak at 1225 cm^{-1}. This suggested the formation of a reactant product between NC and DETA.

Promising EP Toxicity Test results were obtained with heavy metal sludges, chemically converted to their polysulfides, and incorporated at high solids loadings (>72,000 ppm) in polyepoxide binders. The large ratio of toxicant to fixative, and the low volume of the final fixed sludge indicated that polysulfide-epoxy fixatives are more cost-effective than cementitious fixatives. Thus, the total costs estimated for fixing (F) and transporting (T) and disposing (D) of AAP heavy metal sludges utilizing polysulfide-epoxide are approximately 1/16 (F) and 1/10 (T/D), respectively, the comparative costs for the corresponding cementitious-fixed materials. Limited testing of small quantities of Radford AAP NG "slumps" indicated that heavy metal contaminants (lead) present in the residual ash from open burning can also be stabilized by chemical fixation of the metal to the insoluble polysulfide. X-ray diffraction measurements of the heavy metal polylsulfides produced equivocal results regarding their structures.

Commercial ion-exchange resins were evaluated as chemical fixatives for contaminants in simulated AAP sludges. Procedures were developed for successfully fixing lead-containing sludges at pH=5, the pH value at which the simple lead precipitates (hydroxide, carbonate, silicate) normally dissolve. Functional groups which proved particularly effective as chemical fixatives for lead were, in descending order of effectiveness:

Aminodiacetic acid > aminophosphonic (sodium salt) > tertiary amine > sulfhydryl > amidoxime

Two non-ionic exchangers proved to be effective absorbents for TNT and RDX. Although present costs for the resins evaluated ranged from under $3/lb to $14/lb, the potential advantages of these exchangers may offset their high prices. These include (a) simplification of the present wastewater treatment process for heavy metals at AAPs and (b) the potential benefits in lower shipping and storage costs presented by low-volume, highly concentrated "ultimate sludges" produced from these materials.

PREFACE

Contributors to this report include:

    Dr. Eli Mishuck - Project Manager
    Dr. David Taylor - Physical Measurements
    Mr. Rodney Telles - Principal Investigator
    Mr. Hyman Lubowitz - Technical Specialist

Other contributors to the report preparation are:

    Mr. Robert Diehl
    Ms. Marian Carr
    Ms. Cynthia Taylor
    Ms. Evelyn Bentley

TABLE OF CONTENTS

TABLE OF CONTENTS (Continued)

LIST OF ILLUSTRATIONS

LIST OF ILLUSTRATIONS

LIST OF TABLES

LIST OF TABLES (Continued)

1.0 INTRODUCTION

Army Ammunition Plants (AAPs) generally are very large, self-sufficient manufacturing and supply complexes. AAPs often generate their own electricity, steam, and operate wastewater treatment centers.[19,88] Many AAPs engage in a variety of operations involving toxic or otherwise hazardous materials. For example, in operations such as explosives production, load, assembly, and packing (LAP), waste streams are generated that contain significant quantities of contaminants. Treatment of waste streams to remove undesirable constituents often results in the formation of waste sludge. Under the terms of the Resource Conservation Recovery Act (RCRA), most AAP-generated sludges are now classified as hazardous since they are generated from "propellant and explosives manufacture."

The objective of the "Encapsulation/Fixation (E/F) Mechanisms" project was to conduct basic research studies to (1) examine the types of chemical and/or physical bonds which are created in materials during Encapsulation/Fixation (E/F) processing, and (2) ascertain the effectiveness of the resultant products from an environmental standpoint. The study was geared to provide a fundamental understanding of the reaction mechanisms and the basic forces involved in fixation of AAP-type sludges. Additionally, the data generated during the project, by providing the necessary knowledge and understanding, should allow analogous problems to be addressed on a rational technical basis.

---

[19]Forsten, I., "Pollution Abatement in a Munitions Plant," Environmental Science and Technology, Vol. 7, No. 9, pp. 806-810, September 1973.

[88]Thomas, J.C. and Carotti, A., "How the Army Does a Bang-up Job of Treating Effluents," Environmental Science and Technology, Vol. 10, No. 8, pp. 751-756, August 1976.

At the request of USATHAMA, the study was to focus on chemically fixed products over other processes such as microencapsulation or surface encapsulation. Specifically, the work involved several[6,7,8] synthetic sludges representative of military waste sludge types. These were to be treated, preferably, with low-in-cost, readily available E/F agents and by processes which are practical, safe and not energy intensive.

The "Encapsulation/Fixation (E/F) Mechanisms" project consisted of four phases:

Phase I   - Literature/Site Survey

Phase II   - Bench-Scale Studies

Phase III - E/F Product Performance Characteristics Assessment

Phase IV   - Additional Studies*

---

[6]Bartos, M.T. and Polermo, M.R., "Physical and Engineering Properties of Hazardous Industrial Wastes and Sludges, EPA-600/2-77-139, September 1977.

[7]Bell, N.E., Halverson, M.A., Mercer, B.M., "Solidification of Low-Volume Power Plant Sludges," CS-2171, Research Project 1260-20, Battelle Northwest Laboratories, December 1981.

[8]Bender, E.S., Robinson, E.F., Moore, M.W., Thornton, W.D. and Asaki, A.E., "Preliminary Environmental Survey of Holston Army Ammunition Plant, Kingsport, Tennessee," Army Armament Research and Development Command, Aberdeen Proving Ground, MD, Chemical Systems Laboratory, EO-TR-77001, April 1976.

*Phase IV was added as a modification to the contract to provide for additional effort to investigate several related topics not included in the original scope of work.

The ensuing sections of this report describe the work carried out in each of the four phases of the project. Also provided, where appropriate, are discussions on background information and objectives, experimental procedures, apparatus used, tests performed, results, and conclusions and recommendations.

2.0 PHASE I - LITERATURE/SITE SURVEY

A literature review was carried out under Phase I on sludges generated during AAP wastewater treatment and related operations. Eighteen (18) Army Ammunition Plants, two (2) Army Depots, one (1) Arsenal, and one (1) Fort were considered in the survey. No actual site visits were made during this phase. The objectives of the review were set forth in three tasks:

(1) Review Government and open literature sources and compile information describing sludges generated at AAPs,

(2) Examine sludge data to identify potential candidate sludges to be studied under Phases II and III, and

(3) Select sludge compositions for detailed study.

In addition, the results of this survey were intended to provide:

(4) The basis of a rationale for selection of fixatives and E/F processes for the sludges, and

(5) A Test Plan for the Phase II bench-scale studies.

Generally, it was found that literature sources published prior to about 1975 did not provide adequate sludge characterization data. More recent publications, however, describe sludges in sufficient detail to identify a number of potential candidate sludges for study.

The technical approach selected to accomplish Task 1 involved systematic, computer-assisted literature searching. Major data bases included NTIS (National Technical Information Service), DTIC (Defense Technical Information Center, formerly DDC), ENVIROLINE, POLLUTION

ABSTRACTS, APAP Technical Data Base (Army Pollution Abatement Program Technology Support Center, Huntsville), and Technical/Special Reports furnished by the Government.

In examining sludge data under Task 2, above, it was found that AAP-generated sludges and related wastes of interest could be organized under two major categories. The first category, AAP-Generated Sludges Sufficiently Characterized for Possible Study, is described in Section 2.1. From this category, synthetic sludge compositions were selected for detailed study as discussed later in Section 3.1. The second category, AAP-Generated Sludges and Related Wastes of Uncertain Composition, are described in Section 3.2. Although these latter wastes are considered potentially treatable by E/F processes, they were insufficiently characterized for consideration on this project.

Literature Search Methods

To obtain background information on sludge sources and compositions at Army Ammunition Plants (AAPs)[*], a comprehensive literature search was carried out. The effort was initiated through a computerized literature search using the various data bases just described and appropriate key words. Initially, information was obtained by searching two major data bases, NTIS and DTIC. Key words employed in the search included the following:

NTIS Data Base (Includes DTIC)

Army and Waste and Stabilization or Solidification
Pozzolanics
EPA and Encapsulation
DTIC and Encapsulation

---

[*]The literature search was extended to include Army Depots, Arsenals and Forts, as well as AAPs, when it became apparent that these sources also provided relevant information on sludges.

Army and Encapsulation and DTIC or EPA
Microencapsulation
Army and Munition or Munitions and Encapsulation and Ammunition
    and Waste or Wastewater
Army and DTIC and Fixation and Waste
DTIC or EPA and Fixation
Army Ammunition Plants
Sludge Treatment
Army and Hazardous Material
Army and Solid Waste and Ammunition Production
Ammunition and Production or Manufacture
DTIC and Coagulants

The data base POLLUTION ABSTRACTS was also searched. The
following key words were used:

Army and Sludge Disposal or Sludge Treatment
Ammunition Plants
Chemical Fixation
Army and Ammunition

The data base ENVIRONLINE was also searched. Key words used in
this search were as follows:

Army and Sludge Disposal or Sludge Treatment
Army and Ammunition
Electroplating Waste
Army and Chemicals and Wastes

Additional sources and documents were obtained from the APAP
Technology Support Center which had established a data file of printed
material relevant to pollution abatement technology. Finally, sludge
and E/F information were obtained from various Government reports and
documents. References are listed in alphabetical order in Section 7.0
of this report.

2.1 AAP-GENERATED SLUDGES SUFFICIENTLY CHARACTERIZED FOR POSSIBLE STUDY

Literature describing AAP-generated sludges was examined thoroughly in order to identify sludges best suited for study under Phases II and III. A primary criterion in this screening was whether detailed chemical characterizations were reported in the literature. Sludges which were only partially characterized [e.g., by parameters such as pH, Chemical Oxygen Demand (COD), Biological Oxygen Demand (BOD), Total Organic Carbon (TOC), Total Suspended Solids (TSS), Total Solids (TS)], as reported in some Environmental Impact Statements and pollution abatement reports, were not considered sufficiently definitized. In addition, two other major factors were considered during the screening process:[14] (1) volume of sludge generated, and (2) severity of the problem. For example, dilute sludges generated in very small quantities or in isolated cases, such as the powerhouse precipitate sludges generated at Indiana AAP, were excluded. Also, in instances where several sources were available, the most current report was considered authoritative.

Information was gathered concerning twenty-two Army facilities (eighteen AAPs, two depots, one arsenal, and one fort). Of the sludges screened, eleven were considered best suited as potential candidates for study under Phases II and III. Two sludges originated at LSAAP (Lone Star); four were from RAAP (Radford); four were from Tobyhanna Army Depot; and one came from Savanna Army Depot. Table 1 summarizes the ten (10) candidate sludges.

---

[14]Cleary, J.G., "NPDES Best Management Practices Guidance Document," Hydroscience, Inc., Knoxville, TN, EPA-600/9-79-045, December 1979.

Table 1

CANDIDATE AAP SLUDGES*

Facility	Process/Sludge Designation	Reference No.	Sludge Composition Data
LSAAP	Wastewater treatment sludge	(68,69)	Appendix A-1
LSAAP	Wastewater treatment sludge	(96)	Appendix A-2
RAAP	NG-1/Alcohol rectification	(96,28)	Appendix A-3
RAAP	NG-2	(96,28)	Appendix A-3
RAAP	SAR	(97,28)	Appendix A-3
RAAP	Biological	(97,28)	Appendix A-3
Tobyhanna AD	Chrome treatment process	(92)	Appendix A-4
Tobyhanna AD	Copper plating	(92)	Appendix A-4
Tobyhanna AD	Tin/lead fluoroborate	(92)	Appendix A-4
Tobyhanna AD	Composite/synthetic	(70)	Appendix A-5 & A-6

----

*Sludge compositions are given in Appendix A.

It should be noted that several other AAPs reported sludge problems similar to those listed in Table 1. For example, Smith, et al.,[82] and Patterson et al.,[63] reported major pollutants in the effluents; however, these sludges were not adequately characterized for the present study. In addition, similar contaminants were reported in sludges from Watervliet Arsenal[95] and Fort Stewart[94] (see Section 3.2 for discussion).

2.2 AAP-GENERATED SLUDGES AND RELATED WASTE OF UNCERTAIN COMPOSITION

During the literature review, many sludges and solid residues were identified but were not included in the Section 2.1 analysis

---

[82]Smith, L.L. and Dickenson, R.L. (Radford Army Ammunition Plant, Hercules, Inc., Radford, VA), Casrazza, J.A. (Picatinny Arsenal), Propellant Plant Pollution Abatement - Engineering Investigation to Develop Optimum Control Measures to Prevent Water Pollution," TR 4818, March 1975.

[63]Patterson, J., Shapita, N.I., Brown, J., Duckert, W., Polson, J., "State-of-the-Art Military Explosives and Propellants Production Industry," Vol. II, Wastewater Characterization Technical Report, The American Defense Preparedness Association, Industrial Environmental Research Laboratory, Cincinnati, OH, EPA-600/2-76-213C, 273 pp., August 1976.

[95]U.S. Army Environmental Hygiene Agency, Sludge Disposal From Industrial Waste Treatment Plant, Watervleit Arsenal, Watervliet, NY, May 14-18, 1979, APAP Project No. D-1533-W, Hazardous Waste Special Study No. 81-26-8204-80, Department of the U.S. Army, Aberdeen Proving Ground, MD, pp. 1-10.

[94]U.S. Army Environmental Hygiene Agency, Hazardous Waste Special Study No. 37-26-0159-81, Ft. Stewart, GA, April 1981, U.S. Department of the Army, Aberdeen Proving Ground, MD (Internal Correspondence), September 28, 1981.

because insufficient chemical characterization information was provided. Chemical composition was a primary criterion in the selection process in Section 2.1. The sludges and residues of uncertain composition fall into four categories:

(1) Sludges not adequately characterized

(2) Probable sludge sources not characterized

(3) Ash from incineration

(4) Ash from open burning

Sludges not adequately characterized for listing under Section 2.1 were reported at several AAPs. These sludges are identified by sources, as presented in Table 2. An example in the table of an inadequately characterized sludge is the one associated with sulfuric acid production at Volunteer AAP.[67] For all sludges in this category, complete characterizations were not available and disposal practices were not identified. Sources are identified by underlining known sludges in Table 2.

Also included in Table 2, but not underlined, are suspected sludge sources obtained by review of process effluent treatment methods.[62] At most AAPs, these effluent treatments are

_____

[67]Ribaudo, C., Campbell, C., Bulusu, S., Fisco, W., Chen, T.H., "The Chemical Characterization of Pollutants in Waste Water From Volunteer Army Ammunition Plant," U.S. Army Armament Research and Development Command, Large Caliber Weapons Systems Laboratory, Dover, NJ, Technical Report ARLCD-TR-81028.

[62]Patterson, J., Shapita, N.I., Brown, J., Ducker, W., Polson, J., "State-of-the-Art Military Explosives and Propellants Production Industry," Vol. II, Wastewater Characterization Technical Report, The American Defense Preparedness Association, Industrial Environmental Research Laboratory, Cincinnati, OH, EPA-600/2-76-213C, 273 pp., August 1976.

Table 2

IDENTIFICATION OF AAP-GENERATED SLUDGES AND
SOLID WASTES OF UNCERTAIN COMPOSITION*

AAP	Sludge Source	Ash Source	Comments
Badger	Sulfuric acid manufacture; Solventless propellant; Nitroglycerin; Nitric acid concentration; Nitrocellulose; Ball powder manufacture	Open burning: Explosives wastes	Significant sludge source - need further study
Cornhusker	Pink water from load lines	Open burning: Explosives wastes	Production status unknown
Holston	Sodium nitrate process effluent; Nitric acid concentration; Acetic acid and acetic anhydride (RDX-HMX manuf.) concentration and refining; Water treatment;	Open burning; General wastes; Sodium nitrate sludge; Explosive Sediment	Significant sludge source - current treatments unknown
Iowa	Explosive loading strip tanks Kill tanks-lead	Open burn: Pink water; Spent carbon explosive waste; MP FAB IWTS sludge	Heavy metals present
Indiana	Powerhouse precipitate	Open burn: Explosives wastes; Black powder wastewater sediment	Nitrocellulose fines identified: need more information on disposal methods of effluent from acids and propellant manufacture.
Joliet	Sulfuric acid manufacture Nitric acid concentration; Sellite manufacture	Incinerate: Red water (TNT); Pink water (TNT); RDX	

Table 2 (Continued)

AAP	Sludge Source	Ash Source	Comments
Kansas	Pressed explosive manu-facture; Explosive process wastes	N/A	Heavy metals; Pink water - need more information
Louisiana	Pink water (TNT); MP FAB Sludge	Open burn: Explosive waste oils	Metal plating wastes: need more data
Longhorn	Pyrotechnics; Propellant manufacture	Open burn: Explosive waste oils	Metals present
Lake City	Nitrification primers; Explosives primer manufacture; Explosive process wastes	N/A	Heavy metals present
Lonestar	Pink water (TNT) Rework cartridges Metal plating	Open burn: Explosive WTF Sludges	Heavy metals present
Milan	Pink water (TNT); Boiler plant	Open burn: Wastewater settling pits; Explosive waste	Metals present, need further study
Newport	Sulfuric acid; Nitric acid Concentration (Combined sludge)	Incinerate: Red water (TNT)	Significant sludge problem
Riverbank	Metal parts manufacture	N/A	Heavy metal sludge
Scranton	Shells; Projectiles, Forgings, Scale removal cooling	N/A	Heavy metal sludge
Tobyhanna Army Depot	Plating and Metal Finishing	N/A	Heavy metals present

TABLE 2 (Continued)

AAP	Sludge Source	Ash Source	Comments
Twin Cities	N/A	Open burn: Explosive water	Dumping of metal plating waste; Need current treatment infor- mation
Volunteer	Sulfuric acid; Nitric acid concentration; Sellite manufacture	Incinerate: Red water (TNT)	Significant sludge source; Need further study

N/A = Not Applicable

*References for Table: 41, 36, 49, 59, 63

Underlining signifies a known sludge source.

of solids separation,[79] and the available literature does not discuss disposal practices for the separated waste solids. Therefore, wastes stemming from processing the above-mentioned effluent treatments are considered possible sludge sources. These types of sludges are listed in Table 2 by manufacturing process or product source.

Some of the identified sludges and the suspected sludge sources contain heavy metal constituents as listed under the "comments" column in Table 2.

Table 2 identifies two types of ash sources: (1) ash from incineration, and (2) ash from open burning. At most AAPs, red water effluent was incinerated.[88,101] The chemical composition of any resultant ash was not reported. Open burning of contaminated explosive wastes from spent chemical solutions often produces ash. Chemical compositions for this ash are also lacking in the literature. Both types of ash residuals are listed in Table 2, and the waste source is identified. For example, Cornhusker AAP burns various wastes contaminated with explosives in the open.

This table was designed for use as an overview of AAP-generated sludges and ashes. To the greatest extent possible, all sludges were identified by the process from which they originated (e.g., sulfuric

---

[79]Sandmann, H., "Modern Methods of Effluent Treatment," Brown Boveri Review, Vol. 64, No. 3, pp. 174-179, March 1977.

[88]Thomas, J.C. and Carotti, A., "How the Army Does a Bang-up Job of Treating Effluents," Environmental Science and Technology, Vol. 10, No. 8, pp. 751-756, August 1976.

[101]Wheelock, T.D., "Disposal of RAAP Wastewater Treatment Sludges by Incineration," Phase I, Final Report, Chemical Engineering Department and Engineering Research Institute, Iowa State University, Ames, Iowa, April 30, 1982.

acid concentration, nitric acid concentration, etc.). When process
description information was not provided or when sludges were mentioned
in the literature but no process was identified, the sludge or ash was
identified on the basis of the available data.

In compiling information for this table, many discrepancies were
noted. To a large extent, these discrepancies involved the current
status of AAP activities, production, and treatment procedures. When
data were in conflict, a conservative approach was used. For example,
there was conflicting information regarding current production at
Cornhusker AAP. The conservative assumption was made that all
production processes identified in the literature were still in
operation.

3.0 RATIONALE FOR SELECTION OF AAP SLUDGES, ENCAPSULATION/FIXATION (E/F) MATERIALS, AND CHARACTERIZATION METHODS

This section sets forth the rationale for selection of AAP sludge compositions, E/F materials, and characterization methods for conducting Phases II and III of the project. Section 3.1 specifies candidate synthetic sludge compositions and proposes a method of study. Section 3.2 discusses the rationale for selection of E/F materials. Finally, the approach, which was selected for investigating chemical/physical bonds formed during E/F-sludge treatment and their resistance to leaching stresses, is presented in Section 3.3.

3.1 SYNTHETIC AAP SLUDGES SELECTED AND THE RATIONALE FOR SELECTION

The literature review discussed in the previous section resulted in the identification of potential candidate AAP-generated sludges for study under Phases II and III of the project. Examination of sludge compositions showed that most AAP sludges contained similar types of toxic components in combination with other relatively harmless and inert materials. The toxicants consisted primarily of heavy metals and, to a lesser extent, organic compounds such as nitrocellulose. The inert materials were derived from neutralizing/coagulating/precipitating ingredients (e.g., gypsum, lime) used in processing.

Heavy metals have also been reported as the primary toxicants in sludges from industrial operations similar to those which take place at AAPs. For example, work sponsored by EPA and conducted by the U.S. Army Corps of Engineers (Waterways Experiment Station) has involved assessment of the efficiency of E/F processes for managing industrial

sludges which are similar in composition to those in the present investigation.[35,38,42,86,91]   Waste sludges produced in operations such as electroplating, paint pigment production, and metal finishing have been

[35]Josephson, J., "Immobilization and Leachability of Hazardous Wastes," Environmental Science and Technology, Vol. 16, No. 4, pp. 219-223, 1981.

[38]Landreth, R.E. and Mahloch, J.L., "Chemical Fixation of Wastes," Industrial Waste Engineering, pp. 16-19, July/August 1977.

[42]Mahloch, J.L., "Leachability and Physical Properties of Chemically Stabilized Hazardous Wastes," Environmental Effects Laboratory, U.S. Army Engineer Waterways Experiment Stations, Vicksburg, MS, February 1976.

[86]Swope, G.H. (Waste Management and Pollution Control), "Hazardous Waste Discussed at International Meeting of Chemical Societies, Industrial Wastes, Vol. 25, No. 5, pp. 26-28, August/September 1979.

[91]U.S. Army Engineering Waterways Experiment Station, Environmental Laboratory, "Survey of Solidification/Stabilization Technology for Hazardous Wastes," Vicksburg, MS, EPA-600/2-79-056 (PB-299-206) July 1979.

treated by various E/F processes and compared for relative effective-
ness.[33,34,42,44,52]   Shake and column leaching tests historically
have focused primarily upon the rate of loss of the most toxic,

[33]Jones, L.W., Malone, P.G., Thompson, D.W., Meyers, T.E.,
Chemical Fixation of Hazardous Industrial Wastes, U.S. Army Waterways
Experiment Station, Vicksburg, MS, presented at American Institute of
Chemical Engineers 71st Annual Meeting, November 1978.

[34]Jones, L.W., Malone, P.G., Meyers, T.E., Field Investigation of
Contamination Loss from Chemically Stabilized Sludges, U.S. Army
Waterways Experiment Station, Vicksburg, MS, Presented at the Sixth
Annual Symposium on Treatment and Disposal of Hazardous Waste,
EPA-600/9-80-010, March 1980.

[42]Mahloch, J.L., "Leachability and Physical Properties of
Chemically Stabilized Hazardous Wastes," Environmental Effects
Laboratory, U.S. Army Engineer Waterways Experiment Stations,
Vicksburg, MS, February 1976.

[44]Malone, P.G., Mercer, R.B., Thompson, D.W., The Effectiveness
of Fixation Techniques in Preventing the Loss of Contaminants from
Electroplasting Wastes, First Annual Conference on Advance Pollution
Control for the Metal Finishing Industry, Lake Buena Vista, FL, January
17-19, 1978, EPA-600/8-78-010, May 1978.

[52]Meyers, T.E., Francinques, N.R., Thompson, D.E., Malone, P.G.,
Chemically Stabilized Industrial Wastes in a Sanitary Landfill
Environment, U.S. Army Engineering Waterways Experimental Station,
presented at the Sixth Annual Symposium on Treatment and Disposal of
Hazardous Waste, EPA-600/9-80-010, March 1980.

unalterable, and persistent sludge constituents, mainly heavy metals.[45,46,53,60,89] In wastes such as these, where toxicity is often related to the elemental nature of waste constituents [e.g., maximum allowable concentrations of chromium and cadmium in drinking water are 0.05 ppm and 0.01 ppm, respectively;[58] and many of the

---

[45]Malone, P.G., Jones, L.W., Shafter, R.A., and Larson, R.J., Estimation of Pollution Potential of Industrial Waste from Small-Scale-Column Leaching Studies, presented at the Seventh Annual Research Symposium on Land Disposal of Municipal Solid and Hazardous Waste and Resource Recovery, March 16-18, 1981, Philadelphia, PA.

[46]Malone, P.G. and Larson, R.J., Scientific Basis of Hazardous Waste Immobilization, ASTM D-34, Second Annual Symposium on Testing of Hazardous and Industrial Solid Waste (Poster Session), Lake Buena Vista, FL, January 1981.

[53]Mercer, R.B., Malone, P.G., Broughton, J.D., "Field Evaluation of Chemically Stabilized Sludges," U.S. Army Engineering Waterways Experiment Station, Vicksburg, MS, EPA-600/9-78-016, pp. 357-365, September 1978.

[60]Neely, N.S., Walsh, J.S., Gillespie, D.P., Schauf, F.J., Remedial Actions at Uncontrolled Hazardous Waste Sites, SCS Engineers, presented at the Seventh Annual Research Symposium on Land Disposal of Municipal Solid and Hazardous Waste Recovery, Philadelphia, Pennsylvania, March 1981.

[89]Thompson, D.W., "Elutriate Test Evaluation of Chemically Stabilized Waste Materials," Environmental Laboratory, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS, EPA-600/2-79-154, September 1974.

[58]National Academy of Sciences, National Academy of Engineering, Water Quality Criteria, 1972, "A Report of the Committee on Water Criteria," EPA-RF-73-033, U.S. Environmental Protection Agency, Washington, D.C., 594 pp., 1972.

heavy metals are believed to manifest teratogenic disorders at even lower concentrations,[37]] E/F treatment is the preferred disposal option.[46,48]

In the present investigation, primary emphasis was placed upon examining the chemical/physical bonds formed between major toxic constituents of AAP sludges and E/F materials because their stability ultimately determines the effectiveness of the encapsulation process.

3.1.1 Synthetic Sludges

A comparative analysis was made of the AAP sludges reported in Section 2.1 in order to select candidate sludge compositions for basic study. Important criteria in the analysis included the following:[6]

- Volume of sludge generated

- Status of disposal problem

- Availability of other potential disposal options

- Chemical composition of sludge

- Level of toxicity of components

- Chemical/physical properties of sludge (e.g., solubility, homogeneity, viscosity, reactivity of components)

---

[37]Kurtzel, R.B. and Certulo, C., "The Effect of Environmental Pollutants on Human Reproduction, Including Birth Defects," Environmental Science and Technology, Vol. 15, No. 6, pp. 626-640, 1981.

[6]Bartos, M.T. and Polermo, M.R., "Physical and Engineering Properties of Hazardous Industrial Wastes and Sludges, EPA-600/2-77-139, September 1977.

[46]Malone, P.G., op. cit.

[48]Malone, P.G. and Meyers, T.E., Stabilization/Solidification of Waste from Uncontrolled Disposal Sites, presented at the EPA National Conference on Management of Uncontrolled Hazardous Waste Sites, Washington, D.C., October 1980.

Our analysis indicated that these sludges could be readily stabilized/solidifed.[7,14,17,20,32,33,40,47,48,91,102] However, estab-

[7]Bell, N.E., Halverson, M.A., Mercer, B.M., "Solidification of Low-Volume Power Plant Sludges," CS-2171, Research Project 1260-20, Battelle Northwest Laboratories, December 1981.

[14]Cleary, J.G., "NPDES Best Management Practices Guidance Document," Hydroscience, In., Knoxville, TN, EPA-600/9-79-045, December 1979.

[17]Duvel, Jr., W.A., Gallagher, W.R., Knight, R.G., Kolance, J.R., McRalen, R.J., "State-of-the-Art of FGD Sludge Fixation," Final Report, EPRI-FP-671, January 1978.

[20]Fung, R., "Protective Barriers for Containment of Toxic Materials," Pollution Technology Review No. 67, Noyes Data Corp., 288 pp., 1980.

[32]Jeffus, M. and Kerr, R., "Manual of Practice: The Disposal of Combined Municipal/Industrial Wastewater Residues (Metals)," EPA 600/2-79-052, February 1979.

[33]Jones, L.W., Malone, P.G., Thompson, D.W., Meyers, T.E., Chemical Fixation of Hazardous Industrial Wastes, U.S. Army Waterways Experiment Station, Vicksburg, MS, presented at American Institute of Chemical Engineers 71st Annual Meeting, November 1978.

[40]Lubowitz, H. and Wiles, C., Management of Hazardous Waste by Unique Encapsulation Processes, presented at the 7th Annual Research Symposium on Land Disposal of Municipal and Hazardous Waste and Recovery, EPA, Philadelphia, PA, March 1981.

[47]Malone, P.G., and Francinques, N.R., Solidification/ Stabilization as a Technique for Treating Hazardous Wastes, Water Supply and Waste Treatment Group, Environmental Engineering Division, Environmental Laboratory, U.S. Army Engineering Waterways Experiment Station, Vicksburg, MS, prepared for the 24th Annual Meeting of the Mississippi Water Pollution Control Association, April 23-24, 1981, Jackson, MS.

[48]Malone, P.G., op. cit.

[91]U.S. Army Engineering Waterways Experiment Station, Environmental Laboratory, "Survey of Solidification/Stabilization Technology for Hazardous Wastes," Vicksburg, MS, EPA-600/2-79-056 (PB-299-206) July 1979.

[102]Wiegele, G.L., "The State-of-the Art of Waste Disposal Technology," Consulting Engineer, Vol. 55, No. 3, pp. 99-102, September 1980.

lishing _directly_ whether the toxic constituents have become actually chemically fixed (as opposed to indirectly measuring leachate) was considered to be more technically difficult. A major problem in selecting raw sludges and E/F materials for study is the complexity of the combined systems. For example, the multiple phases and compounds present in the sludge-fixative mixtures could mask analytical measurements and severely limit the examination of discrete chemical/physical bonds created between toxicant and fixative. Additionally, in order to enhance the probability of chemical fixation, molecular dispersion of sludge components in E/F materials is of primary concern, as discussed in Section 3.2. Poor reproducibility of raw sludges from batch to batch, biological activity which can alter some sludge compositions, and other uncontrolled factors would adversely affect our ability to carry out some of the more subtle yet critical analytical measurements essential to this investigation.

Thus, in order to investigate the chemical/physical bonds created between toxicants in sludges and E/F materials, a stepwise approach was developed which employed synthetic sludges. The aim of the approach was to establish, first, the nature of the bonds formed between discrete toxicants and E/F binders. Second, examination would be made of the effect on bonding caused by the presence of other constituents in the sludge. Research with synthetic sludges, as opposed to real sludges, can provide more reliable and reproducible data which, along with controls, permits a better sorting out of the E/F bonding phenomena. [On the other hand, real sludges may contain constituents which are either unknown or difficult to simulate.]

Table 3 summarizes the major inorganic and organic toxicants present in each of the potential candidate AAP-generated sludges discussed in Section 2.1. Comparison showed, however, that several toxicants were common to most sludges and/or were present at relatively higher concentrations. These contaminants were:

Table 3

SUMMARY OF MAJOR TOXICANTS PRESENT IN POTENTIAL CANDIDATE
AAP-GENERATED SLUDGES IDENTIFIED IN SECTION 2.1

Facility	Sludge Designation/Process	Major Toxicants
LSAAP	Wastewater Treatment Sludge	Pb, Ni, Mn, Cr
LSAAP	Wastewater Treatment Sludge	Pb
RAAP	NG*-1/Alcohol Rectification	NC**, CN, Pb
RAAP	NG-2	Pb
RAAP	SAR	Mg
Tobyhanna AD	Cr Treatment Process	Cu, Cr, Cd, Pb
Tobyhanna AD	Copper Plating	Cu, Pb, Cd, Cr
Tobyhanna AD	Tin/Pb Fluoroborate Solution	Pb, Cu, Cd, Cr, Be
Tobyhanna AD	Synthetic Plating Samples	Cr, Zn, Cn, Ni, Pb
Savanna AD	Lead Azide Process (Iowa AAP Process)	Pb (insol. compounds), Pb (metal)

*Nitroglycerine
**Nitrocellulose

- Lead, chromium and cadmium

- Nitrocellulose (NC)

It is noteworthy that these contaminants were also reported to be present in wastes generated at several other military installations.[8,67,81,82,85,93] For example, Lake City, Longhorn, Indiana, and Badger AAPs were reported to have similar pollutants present in

---

[8]Bender, E.S., Robinson, E.F., Moore, M.W., Thornton, W.D., and Asaki, A.E., "Preliminary Environmental Survey of Holston Army Ammunition Plant, Kingsport, Tennessee," Army Armament Research and Development Command, Aberdeen Proving Ground, MD, Chemical Systems Laboratory, EO-TR-77001, April 1976.

[67]Ribaudo, C., Campbell, C., Bulusu, S., Fisco, W., Chen, T.H., "The Chemical Characterization of Pollutants in Waste Water From Volunteer Army Ammunition Plant," U.S. Army Armament Research and Development Command, Large Caliber Weapons Systems Laboratory, Dover, NJ, Technical Report ARLCD-TR-81028.

[81]Smith, L.L. and Dickenson, R.L. (Radford Army Ammunition Plant), and Pregren, E.R. (Picatinny Arsenal), "Engineering Study of Disposal Methods for Waste Acid Neutralization Sludge," TR 471, November 1973.

[82]Smith, L.L. and Dickenson, R.L. (Radford Army Ammunition Plant, Hercules, Inc., Radford, VA), Casrazza, J.A. (Picatinny Arsenal), Propellant Plant Pollution Abatement - Engineering Investigation to Develop Optimum Control Measures to Prevent Water Pollution," TR 4818, March 1975.

[85]Stevens, B.W. and McDonnel, R.P. (Rohm and Haas Company, Philadelphia, PA), Andren, R.K., Nystrom, J.M. (U.S. Army Natick Development Center, Natick Massachusetts), Explosives Removal from Munitions Wastewaters, presented at the 30th Annual Purdue Industrial Waste Conference, May 6-8, 1975.

[93]U.S. Army Environmental Hygiene Agency, U.S. Department of the Army, Hazardous Waste Management Consultation No. 37-26-0150-81, Savanna Army Depot Activity, Savanna, IL, April 1981, Aberdeen Proving Ground (Internal Correspondence), August 1981.

their waste effluents. However, specific chemical data concerning these effluents were not provided in the literature, as discussed in Section 2.2. In addition, plating sludges at Watervliet Arsenal and caustic baths at Fort Stewart, Georgia, were reported to contain pollutants such as chromium, lead, nickel, zinc, cadmium, and lead, chromium, selenium, respectively.

Table 4 lists the candidate synthetic sludges selected for study in Phases II and III. These consist of inorganic/wet sludge, organic/dry sludge, inorganic/dry sludge, and organic/wet sludge, as defined below.

Synthetic Sludge	Description
Inorganic/Wet (Aqueous Solution - Suspension	Inorganic toxicant(s) dispersed or dissolved in water
Organic/Dewatered or Dry	Organic toxicant(s) dewatered or dried and containing no free water
Inorganic/Dewatered or Dry	Inorganic toxicant(s) dewatered or dried and containing no free water
Organic/Wet (Aqueous Solution - Suspension	Organic toxicant(s) dispersed or dissolved in water

Furthermore, the literature survey revealed, as would be expected, that wet sludges when mixed with (1) organic polymeric binders/fixatives such as bitumens* or (2) organic polymerizable fixatives such as urea formaldehyde result in inhomogeneous and spongy products.[65] In order to promote chemical fixation, intimate

----

[65]Pojasek, R.B., Toxic and Hazardous Waste Disposal, Vol I, Processes for Stabilization/Solidification, Ann Arbor Science, Inc., Ann Arbor, MI, 1979.

*Some processes consist of mixing wet waste and bitumen or bitumen emulsion followed by drying prior to disposal.[8]

[8]Bender, op cit.

Table 4

SYNTHETIC SLUDGES SELECTED FOR PHASES II AND III

Sludge Designation	Sludge Type/Form	Major Toxicants in Sludge	Parameters Which May Be Varied During Study
A	Inorganic/Wet Aqueous Solution - Suspension	Pb, Cr, Cd	
B	Organic/Dewatered or Dry	NC	Toxicant Concentrations, presence of inerts (diluents) and other sludge ingredients, E/F agent type, complexity and concentration.
C	Inorganic/Dewatered or Dry	Pb, Cr, Cd	
D	Organic/Wet Aqueous Solution - Suspension	NC	

contact between fixative and toxicant was accomplished by selecting compatible mixes composed as follows:

Synthetic Sludge	Compatible Fixative
Inorganic/Wet (Aqueous Solution - Suspension)	Inorganic Binder
Organic/Dewatered or Dry	Organic Binder
Inorganic/Dewatered or Dry	Organic Binder
Organic/Wet (Aqueous Solution - Suspension)	Inorganic Binder

as discussed in Section 3.1.3, below.

3.1.2 Practical Considerations on Use of Dried Sludges

3.1.2.1 Flammable Toxicants

AAP sludges containing explosive or flammable materials such as nitrocellulose (NC) should not be dried by procedures in which friction and/or heat can cause catastrophic explosions or fires. It is unclear as to whether dilution of NC by 80 percent inorganic ingredients, such as in RAAP NG-1 sludge shown in Appendix A-3, will inhibit or prevent these untoward events from occurring. It has been reported that certain "reductant" solutions containing oxalic acid and/or other compounds containing the elements CHON may be used to desensitize explosives such as NC, TNT, RDX, NG, and other sensitive materials.[74]

---

[74]Roth, M., "Non-Polluting Process for Desensitizing Explosives," AD D006421, 18 December 1978.

27

It was decided to investigate -- on a small scale and with adequate safety precautions -- whether NC fines, dispersed or dissolved in a polymerizable organic binder, can be chemically fixed by the binder. It is conceivable that the NC may also become desensitized and less flammable by this E/F procedure.

3.1.2.2 Cost Implications and Benefits

3.1.2.2.1 Preliminary Cost Estimates

Dewatering and drying of AAP sludges is an energy-intensive procedure. Reported costs for dewatering sludges containing over 95 weight percent water to 25 weight percent solids by centrifugation or vacuum filtration are $35 and $39 per ton, respectively.[90] These costs include both variable operating costs and fixed costs for recovery of capital investment, taxes and insurance. Total costs to reduce the water content of biological sludges from 95-99 percent water to 1-5 percent water by wet air oxidation at a 5 tons/day Sludge Handling Facility have been reported as $54 to $64 per ton.[13] A four-cycle flash drying system used to dry sludge for use as fertilizer, at a production capacity of up to 150 tons/day, produces material with 5 percent moisture from a feed containing 96 percent water at $21/ton [in 1972 dollars].[66]

An independent estimate of the costs for reducing the water content of an AAP-type sludge from 75 percent weight to 1 weight

---

[90]Unit Operations for Treatment of Hazardous Industrial Wastes, Pollution Technology Review, No. 47, pg. 326 (Table 3), pg. 495 (Table 2), D.J. DeRenzo, Editor, Noyes Data Corporation, New Jersey, 1978.

[13]Cheremisinoff, P. and R. Young, Pollution Engineering Practice Handbook, Ann Arbor Science, 1981.

[66]Process Design Manual for Sludge Treatment and Disposal, EPA 625/1-74-006, U.S. Environmental Protection Agency, pgs. 8-22 to 8-26, October 1974.

percent water is $73/ton, including operating costs and amorti-zation.[18] The EPP estimate is based on the use of a Concurrent Rotary Drier with a capacity of 5 ton/day; operating costs are $20/ton using steam and electricity; and amortization of $300,000 capital costs is at 10 percent over 5 years, $80,000/year, or $53/ton.[64]

Some additional costs may be necessary to maintain effluent streams and volatiles resulting from the dewatering and drying operations at acceptable environmental levels. These were not included in the estimates.

3.1.2.2.2 Potential Cost Benefits

There appear to be potential cost benefits associated with dewatering/drying liquid wastes prior to solidification that are worthy of consideration. These are best illustrated by reference to the economic analysis reported in the LSAAP report on Chemical Fixation of Sludge.[69,pg. 26] The cost of chemical ingredients necessary to fix 300 pounds of LSAAP sludge containing 2 percent solids averages $14 or $93/ton of sludge for the seven (7) compositions shown in Table 7 of that reference.

A quantity of 250 to 300 pounds of fixative was required to treat 300 pounds of sludge, resulting in a total mixture weight of 550 to 600 pounds. Yet the weight of toxicants in the mixture was less than six

---

[18]EPP, Private Communication.

[64]Perry, Robert H. and Chilton, C.H., Chemical Engineers' Handbook, 5th Edition, McGraw Hill, 1973.

[69]Robinson, J., "Chemical Fixation of Sludge: Laboratory Studies," Contractor Report ARLCD-CR-82044, U.S. Army Research and Development Command, Large Caliber Weapon Systems Laboratory, Dover, New Jersey, AD-E400 903, October 1982.

pounds. For comparison, if the sludge had been dried prior to fixing and, say, an equal weight of organic fixative were used, the total weight of fixed sludge would be less than 12 pounds.

The exact allowable quantity of moisture for a "dry" system has yet to be determined. It should depend on factors such as the absorbability of the solids in the sludge and the nature of the organic polymer fixative used. Epoxies containing one percent moisture or less, for example, have been found to cure satisfactorily with no noticeable effect on physical properties.[21] Also, as shown later in this report, Portland cement may be used to absorb water or "chemically dry" wet mixtures.

A number of potential cost benefits of reduced weight (and volume) associated with pre-drying the sludge to between one and five percent moisture include the following:

   (1) Significantly reduced quantity of fixative (should compensate for the higher cost per pound of the organic binder).

   (2) Significantly reduced waste processing volume (and hence the size and cost of the processing plant and equipment).

   (3) Significantly reduced shipping costs.

   (4) Significantly reduced landfill area required for disposal.

In summary, while drying AAP sludges is indeed an energy-intensive process, the potential cost benefits to be gained from the significant reductions in volumes of fixative required and fixed waste produced are noteworthy and should be considered further.

----

[21]Glowacki, A.S. and MacDonald, D.C., "Protective Coatings for Application in Submersible Vessels, AD-460-364, 1965.

3.1.3 Proposed Method of Study

In order to investigate the nature of the physical/chemical bonds created in AAP sludge-E/F products, a systematic method of study was developed. Four sludge types were selected as shown in Table 4. The purpose of initially excluding inert components (i.e., $CaSO_4$, CaO, etc.), solids, and mixtures of organic/inorganic contaminants which are often present in sludges, is to begin with homogeneous systems which are more amenable to basic study. (The issue of homogeneity, and its probable role in chemical fixation, is discussed later in Section 3.2) In addition, difficulties introduced in fixing inorganic/organic waste mixtures are avoided.[48] Homogeneous toxicant/fixative mixes would be examined first to investigate the E/F material's role in chemically fixing toxic constituents. Once bonding was demonstrated for the binary compositions, a baseline of data would be developed for assessing effects on bonds due to the presence of inert materials and other actual AAP sludge ingredients.

It should be pointed out that AAP waste residues appear in both sludge and ash form. Whereas the present project was concerned exclusively with sludges, the literature search has indicated increasing activity in incineration as a means of both destroying organic compounds and concentrating the hazardous wastes. In addition, open burning of spent carbon-containing adsorbed nitrobodies associated with production of NG, TNT, HMX/RDX, and other hazardous materials is still practiced at a number of AAP plants. Ash generated from open burnings may contain incompletely combusted active material (verbal communication, AEHA).

An extended project is depicted in Figure 1 which includes the synthetic AAP sludges presently under investigation and illustrates additional effort with actual sludges and ash residues.

---

[48]Malone, P.G., op. cit.
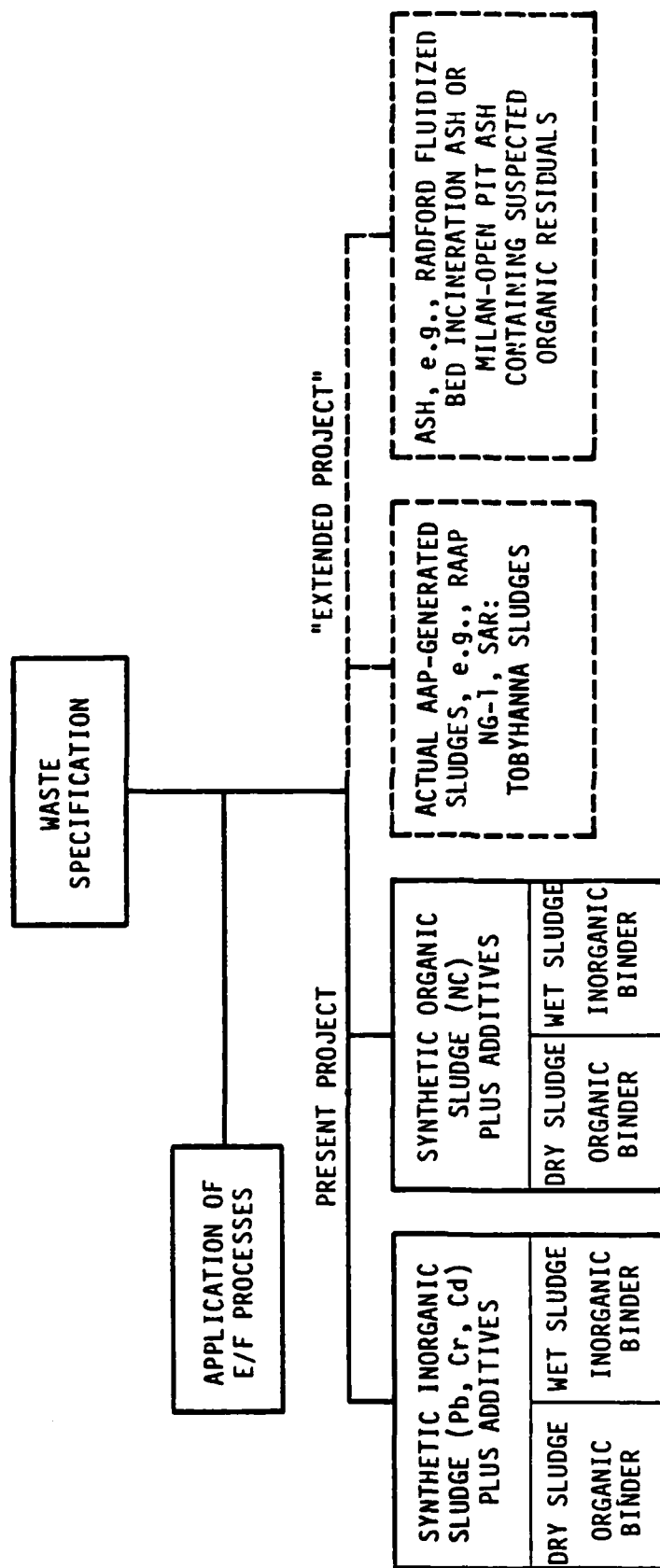
Figure 1. Proposed Project for Investigation of Physical/Chemical Bond Formation in AAP-Type Wastes.

3.2 CANDIDATE FIXATION MATERIALS AND PROCESSES

The literature survey conducted in Phase I of this project indicated that representative AAP sludges generally contain metallic contaminants such as Pb, Cr, Cd; organic materials such as NC, nitrobodies derived from NG and TNT, cyanides, and miscellaneous breakdown products from metallo-organic compounds, solvents, wetting agents, etc.; and salts from neutralization, precipitation, flocculation, and scrubbing operations.

Metallic contaminants represent the ultimate sludge and are most suitable for recovery or fixation. Organic contaminants may be recovered, processed further by chemical conversion, incinerated, or fixed. Volatile, liquid, oil-like, unstable, stable but highly toxic organic compounds (such as PCBs) are normally not considered good candidates for fixation. Nitrocellulose falls into a category where recovery, incineration and fixation represent viable options. Cost considerations and other factors enter into the decision as to the best approach. Data generated by this study may help in arriving at a final decision.

3.2.1 Criteria Affecting Contaminant Fixation

It has been postulated that, in order for successful fixation of contaminants to take place, the contaminants must be embodied in a structure which resists the solubilizing action of the environment in which it is placed, e.g., water action in the earth. Macroscopic physical properties such as bulk density, porosity, permeability and mechanical properties such as rigidity, resistance to shear stress, and viscoelastic behavior represent important parameters affecting rate of solubilization or leaching. However, for structural integrity to be maintained over appreciable time, it is the microscopic and submicroscopic properties at the molecular level that are of prime

33

significance.[5,26] The objective of the present project was to investigate the bonds which are established during the chemical fixation process and to explore the mechanisms of the physico-chemical reactions involved.

Fixatives were selected (a) which presented a high probability of reaction at the molecular level with the toxicants in the candidate AAP sludges identified in the previous section and (b) which were amenable to investigation and characterization by the methods described below.

3.2.2 Candidate Fixatives for AAP Sludges

Polysilicates, amine-cured epoxides, and polysulfides were selected for study as fixatives for contaminants found in AAP sludges. This selection stemmed from an extensive survey of fixatives described in the referenced technical literature. Particular emphasis was placed upon ability to react with contaminants, low cost, availability, ease of processing, and expected physical and mechanical properties. Polysulfides and polysilicates were addressed primarily to fixing toxic metals, and the epoxides to fixing contaminating materials of an organic nature. Nitrocellulose may be reactive with silicates and therefore was to be tested with polysilicates as well as with polyexpoxides.

Toxic metals were fixed by attempting to disperse them into the matrix of the fixatives and chemically bonding them thereto. Thus, for

$$Na_2S_x + MX_2 = MS_x + 2NaX$$

---
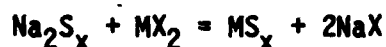
[1]Barney, G.S., "Fixation of Radioactive Waste by Hydrothermal Reactions with Clays," Prepared for U.S. Atomic Energy Commission by Atlantic Richfield Hanford Co., January 1974, 31 pp.

[29]Hattori, M., Yaku, K. Nagaya, K., "Sludge Containing Chromium and Calcium by Heating with Silica," _Environmental Science and Technology_, Vol. 12, No. 13, pp. 1431-1434, 1978.

example, by reacting with polysulfides, metals would be fixed into a sulfur matrix. Sulfur (S_{x-1}), in excess of that required to bond the metal chemically, forms the matrix bearing the contaminant. Thus, sulfur fixes the contaminant and provides the matrix which determines the product's physical and mechanical properties. Elemental sulfur, if required, reacts as follows:

$$MS_x + S_y = MS_{x+y}$$
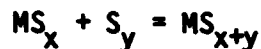
Regarding mechanical performance, sulfur has been used in engineering applications such as road building.[12,41] The mechanical properties of the sulfur products have been characterized and noted to exhibit plastic-type ductile behavior.

Polysilicates have been reported to stabilize metals similarly, i.e., by locking the toxic metals chemically into the matrix. The matrix material in this case is characterized by calcium polysilicate formed by chemical displacement of polysilicate alkali metal by a mixture of calcium salt and mineral acid. The mechanical properties of the cured matrix in this case, however, tend to be brittle rather than plastic.

Options for preparing contaminant fixation products are based on state-of-the-art processing of polysulfides and polysilicates. Polysulfides in combination with sulfur products lend themselves to thermoforming, thereby consolidating the metal polysulfides into monolithic material. Heating is not required with polysilicates or polysulfides. Chemical reagents are employed, instead, to promote consolidation.

---

[12]Chemical Week, "Rebuilding the Market for Highway Repair - A Role for Sulfur," Chemical Week, Vol. 131, No. 22, pp. 55, December 1, 1982.

[41]Ludwig, A.C., "Plasticized Sulfur Asphalt Replacements," Ind. Eng. Chem. Prod. Res. Div., 21, pp. 76-79, 1982.

Other ingredient materials, such as cement, fly ash, lime, and gypsum, would be added to the polysilicate system to simulate LSAAP-treated sludges in view of the promising results reported by Lone Star AAP for these systems.[68,69] The metals in these more complex mixtures may become partially incorporated into the matrix by molecular dispersion, with the remainder of particles dispersed heterogeneously. These products would be nonhomogeneous and thus may present difficulties in studying the basic phenomenon affecting chemical bonding and the stability of contaminants in the fixed products. Heterogeneous products may be expected to exhibit lesser performance than similar but homogeneous products may be capable of providing. This observation can be particularly appreciated with respect to leaching stresses because all metal atoms would not be equally resistant to delocalization; those unaffected by the matrix would be expected to be the more mobile ones. On the other hand, the insolubility of the metal hydroxides or sulfides may be the determining factor in leaching environments such as that provided by the EP Toxicity Test.

Fixation of organic contaminants in AAP sludges is viewed to be parallel to that given above for metals. The epoxide reactants are expected to dissolve the organic contaminants. Hence, amine-cured epoxides would provide an appropriate matrix to effect molecular dispersion of the contaminants. Hydrogen bonding between matrix and contaminant is expected to occur during consolidation and cure of products. This phenomenon should cause enhanced stabilization of the organic contaminants. Furthermore, consolidation can be effected readily because the epoxides cure at room temperature, thus negating need for provisions for heating.

---

[68]Robinson, J., "Chemical Fixation of Sludge," Day and Zimmermann, Inc., Lone Star Division, Texarkana, TX, 32 pp. (undated).

[69]Robinson, J., "Chemical Fixation of Sludge: Laboratory Studies," Contractor Report ARLCD-CR-82044, U.S. Army Research and Development Command, Large Caliber Weapon Systems Laboratory, Dover, New Jersey, AD-E400 903, October 1982.

In addition to being readily formable materials in themselves, amine-cured epoxides were expected to show enhanced stability under leaching conditions. In contrast, organic acid-cured epoxides and thermosetting polyesters give rise to groups potentially hydrolyzable when exposed to water, thereby causing loss of material strength. An additional feature concerns costs, i.e., materials used to prepare amine-cured epoxides are lower in cost and are commercially mass produced.

3.3 MEASUREMENT TECHNIQUES AND IMPLEMENTATION

The techniques for investigating chemical fixation of contaminants and determining the nature of their chemical associations are given in this section. Encapsulated/Fixed waste materials were studied, stepwise, by several different techniques as follows:

3.3.1 Screening Performance of Candidate Test Samples

Preliminary leaching of material was accomplished by taking ground-up material and subjecting it to accelerated leaching by repeated washing with fresh leachate. This should promote dissolution of the waste/binder material if such dissolution were to occur. The resulting solution was filtered and the filtrate analyzed. Atomic absorption spectrometry (AAS), either flame or furnace, was used to determine the toxic metals that may be released. These measurements were designed primarily to screen candidate E/F materials and processes and to select samples for further testing. Desirable samples would resist delocalization of contaminants into solution. Since the solution material consisted of primarily elemental or soluble complex ions, this procedure provided no speciation information on the nature of the matrix or chemical interactions therein. Gas chromatography (GC), infrared (IR) spectroscopy, or other analytical procedures could then be used to analyze for nitrocellulose or other organic materials.

3.3.2 Microscopic Examination of Test Samples

The identification and characterization of acceptably fixed material was the primary purpose of the Phase II work. The first technique to be applied in this effort could be optical microscopy. This technique would screen for sample homogeneity -- the extent to which the sample appears to be uniform. If fixed samples containing contaminants were similar in appearance to the fixative material alone, this might represent an indicator of chemical fixation. Mixing and particle size variations had to be carefully controlled to ensure that these did not create sample inhomogeneities that could be mistaken for a lack of chemical fixation.

Bulk samples were screened "as is," using reflected light. This could be followed at higher magnifications using transmitted light provided the sample could be prepared in layers or, preferably, thinly sectioned. Sectioning, in turn, would depend on the consistency of the material. It was expected that polymeric materials such as the polysulfides or polysilicates could be sectioned.

Illumination utilized standard sources, but polarized light could also be used. This could indicate whether the phases being examined were isotropic to the light source and would provide further evidence of homogeneity.[11] The presence of different phases would be a function of sample uniformity.

3.3.3 Examination With Scanning Electron Microscopy

Although the magnification and resolving power of the optical light microscope is limited, screening of the samples by this means will permit the best candidate mixtures to be isolated. The greater the homogeneity of the sample, the more probable the existence of

---

[11]Chamot, E.M. and C.W. Mason, Handbook of Chemical Microscopy, Vol. 1, 4th Edition, Wiley Interscience, New York, NY, 1983.

chemical bonding. Those samples most promising were subsequently examined using the scanning electron microscope (SEM). The SEM offered several advantages. First, it provided greater magnification so that the uniformity of the sample could be more closely studied.[16] Second, its resolving power is greater so that objects that could not be clearly examined previously could now possibly be identified or at least better characterized.[22] If occlusions or inhomogeneities existed, their size and distribution could be determined.

Prior to SEM analysis, samples would probably need to be coated either with carbon or gold since all waste/binder mixtures are expected to be insulators.[23] This should not affect X-ray sample results since carbon does not provide an X-ray signal that is detectable by most detectors and gold's signal is easily identifiable. Without coating, examination of the samples would be very difficult if not impossible.

3.3.4 Additional Examination Techniques

Through the use of the SEM's accompanying energy-dispersive X-ray analysis capabilities, attempts could be made to map the elemental distribution within the sample. This would provide further information since the X-rays generated by the bombardment of the sample with electrons are emitted at energies characteristic of the different elements. If an element of interest were distributed uniformly, it indicated that the sample was well mixed and/or chemical binding had occurred. If specific sites existed that contained disproportionate quantities of a given metal, this suggested differential properties or chemical reactions. For different synthetic sludges (metals) but the

---

[22]Goldstein, J.I. and Yakowitz, H., Practical Scanning Electron Microscopy: Electron and Ion Microprobe Analysis, Plenum Press, New York, pp. 95-147, 1975.

[23]Goldstein, J.I. and Yakowitz, H., Practical Scanning Electron Microscopy: Electron and Ion Microprobe Analysis," Plenum Press, New York, pp. 213-217, 1975.

same binder, the results or distribution of the metal could change. Mixtures could also give identifiable changes that reflected the extent of chemical reaction that had occurred. This method is effective only for elements above sodium in atomic number and thus is not useful for such wastes as nitrocellulose fines.

In addition to the above techniques, the transmission electron microscope (TEM) could be utilized in an electron diffraction mode. This technique required a crystalline or microcrystalline sample, since the image was generated by the diffraction of electrons by the regular array of atoms within the crystal. By examining the binder before and after mixing and curing with the waste material, it should be possible to determine whether metal ions were incorporated in the crystal lattice, thus providing evidence of chemical interaction. X-ray diffraction would provide comparable information.

3.3.5 Establishing the Nature of Chemical Bonding

Another key instrument to be used during Phase II was the infrared (IR) spectrometer. The vibrational spectra of many of the sulfides and silicates of metals of interest such as Cd, Ni, Zn, Cr, and Mn, have been studied,[72] especially in the far infrared. In addition, metal-oxygen vibrations and interactions between Ca and Al, and oxygen, sulfur and silicon (all expected to be present) are well studied. This should facilitate identification of bonds between the E/F material and the waste. The IR could also offer an opportunity to monitor, dynamically, the "curing" of the mixture by following spectral changes over time. Regardless, there were three possible approaches to obtaining IR spectra. The solidifed material could be ground up or otherwise dispersed in an inert mull; it could be compressed into a metal halide pellet; or else, internal reflection spectroscopy (IRS)/attenuated total reflectance (ATR) spectroscopy could be

---

[72]Ross, D., _Inorganic Infrared and Raman Spectra_, McGraw Hill Company, Ltd., London, 1972, pp. 95-112.

used.[24,80] Several factors affected the choice of one or more of these methods. Specifically:

- The energy region of interest (e.g., where vibrational interactions between elements are most probable),

- The compatibility of the E/F waste with the medium (e.g., unbound water would potentially dissolve the salt crystals used in the pellet approach),

- The physical properties of the sample (e.g., IRS requires good contact with a plate so that a smooth surface is best), and

- The energy throughput obtainable by the method and the sample.

Obtaining the vibrational spectra was facilitated by the use of Fourier transform infrared (FTIR) spectroscopy, which is available at S-CUBED. Use of this technique would facilitate combination of scans, thus enhancing potentially weak signals and helping to remove noise. The spectra could also be manipulated so that background spectra - such as those associated with the original E/F material - could be subtracted or the results ratioed to give spectra more readily interpretable.

In addition to studying metal-to-non-metal bonds in the inorganic systems, the IR technique would also be used as a tool to study hydrogen bonding in the organic systems. If such bonding were to occur in epoxy-nitrocellulose mixtures, for example, there should be observable differences in the spectra. Thus, IR should help establish the extent of chemical interaction in this E/F system.

[24.]Griffiths, P.R., Chemical Infrared Fourier Transform Spectroscopy, John Wiley and Sons, New York, 1975, pp. 137-147.

[80]Smith, D.F., Quantitative FT-IR Spectroscopy of Polymer Surfaces Using Variable Angle ATR, in Digilab Users Conference, June 1980, Digilab, Cambridge, Massachusetts.

4.0 TEST PLAN

4.1 INTRODUCTION AND OBJECTIVES

The Test Plan for the Phase II Bench-Scale Studies consisted essentially of:

(1) Procurement of appropriate inorganic/organic materials required for the E/F experiments.

(2) Preparation of samples and selection of those which presented a good physical appearance for analysis.

(3) Performance of analytical measurements by means of X-ray or electron beam diffraction, internal reflectance IR and other techniques in order to identify any crystal structures or matrices which were formed, thereby providing an insight into the reaction mechanisms involved.

The plan was prepared in accordance with DI-T-5248(M), Test Procedures, as described in the basic Contract.

The rationale for selection of materials, processes and techniques to carry out the test plan was described in the previous Section 3.0. It emphasized chemical fixation and focused on:

(a) Synthetic sludge compositions which typified inorganic and organic contaminants associated with waste products emanating from production and processing activities at Army Ammunition Plants, Arsenals and Depots.

(b) Inorganic and organic fixatives and E/F processes which fixed the contaminants physico-chemically into a product in which the contaminant was immobilized and was resistant to leaching action.

(c) Measurement techniques which permitted investigation of the nature of the chemical and/or physical bonds and the reaction mechanisms involved.

4.2 TECHNICAL APPROACH

4.2.1 Stepwise Approach

The philosophy underlying the test plan was, first, to carry out bench-scale studies with synthetic binary mixtures consisting essentially of the contaminant and the fixative (E/F) material. These were to be compared with the fixative (binder) material cured alone (control) at the same solids loadings as the binary mixture and following the manufacturer's directions when available.

Differences would be sought in the pre- and post-cure characteristics of the control and the binary mixture. Before-cure properties of interest included ease of mixing, homogeneity, viscosity, rate of hardening (or cure) and exothermicity. Post-cure characteristics consisted of observation of gross mechanical properties such as hardness/toughness/elasticity, shrinkage, homogeneity, porosity, chemical stability (e.g., resistance to accelerated leaching), and suitability for investigation of "micro" properties. The latter included physical measurements by means of light microscope, electron microscope, FTIR and other instruments.

The binary mixture should provide a realistic model for investigating the nature, extent and stability of chemical bonds which may have been formed. Simultaneously, it would be utilized to investigate optimization of the recipe, order of addition of ingredients, rate and extent of cure; and it would serve as an indicator of whether the toxicant affects the cure. For example, certain toxicants could catalyze or inhibit the hardening process, thereby requiring compensatory adjustments in the recipe.

Following the investigation of the binary mixture, other ingredients which were representative of components found in real sludges and in the more complex polysilicates would be added in

43

stepwise fashion. Again, investigation would be made of the effects of each additive on pre-cure, post-cure and micro- and macro- properties. Figure 2 illustrates, for an LSAAP-type synthetic sludge, the stepwise approach and build-up from a basic binary to a multi-component system.

4.2.2 Investigation of Binary Mixtures

E/F materials were chosen which were capable of both solubilizing and reacting chemically with the contaminants. Other desirable characteristics of candidate E/F materials included the following:

(1) Chemically identifiable,

(2) Readily available,

(3) Reactive with contaminant under mild conditions to form a solidified structure with desirable physical appearance and handling properties,* and

(4) Compatible with either wet, dewatered or dry systems.

The "cured" binary mixtures containing contaminant and fixative would then be subjected to tests for homogeneity by sequential measurements utilizing instrumentation such as optical microscopy, scanning electron microscopy and scanning electron microscopy with energy-dispersive X-ray analysis, (EDAX). This sequence of tests would allow observation of regions of heterogeneity in the matrix on an increasingly smaller scale and should afford a means for quantification of the degree of molecular dispersion, cluster size and distribution, elemental mapping, and possibly could provide insight into whether chemical reaction or solid solution has occurred. It would also be

---

*May vary from glassy to rock-like to viscoelastic.

SYSTEM	SERIES	SLUDGE	FIXATIVE	PLAN
	I	A. Lead Nitrate (soluble lead)	B. Sodium polysilicate solution calcium nitrate	C. 1. Prepare 50 wt % solutions 2. Cure at neutral pH 3. Examine pre- and post-cure appearance 4. Instrumental measurement of chemical bonds
	II	A. Lead Carbonate (insoluble lead)	B. Same as IB	C. Same as IC 1 through 4 (except for suspended insoluble lead)
	III	A. Lead Nitrate	B. Same as IB	C. Same as IC 1,3,4; 2. Adjust pH 11 to precipitate lead hydroxide
BINARY	IV	A. Lead Salt (based on results of I - III)	B. Sodium polysilicate solution lime	C. Variation of IC - IIIC Plan (based on results of I - III)
	V	Optimum soluble lead systems from I, IV		C. Variation of IVC Plan
	VI	Optimum insoluble lead systems from II, III, IV		C. Variation of IVC Plan
MULTI-COMPONENTS (Sludge)	VII	A. V plus Diatomaceous Earth (inert additive)	B. Same as IB	C. Same as IC Several concentrations of diatomaceous earth
	VIII	A. VI plus Diatomaceous Earth (inert additive)	B. Same as IIB or IIIB	C. Same as II or IIIC Several concentrations of diatomaceous earth
	IX	A. VI and/or VII plus Calcium Sulfate	B. Same as VIB and/or VIIB	C. Variation of VIC and/or VIIC
	X	Optimum systems for VI - VIII		C. Variation of VIIIC Plan
	XI	IX plus stepwise additions of other lead salts, calcium salts, cadmium nitrate, chromium oxide, iron chloride, etc.		C. Variation of IXC Plan
MULTI-COMPONENTS (Fixative)	XI	A. Same as IVA	B. IVB plus Portland Cement Type I	C. Variation of IVC Several concentrations of Portland Cement
	XII	A. Same as IVA	B. XIB plus fly ash	C. Variation of XIC Several concentrations of fly ash
MULTI-COMPONENTS (Sludge and Fixative)	XIII	Varying combinations of Series VI - X with XI - XII		C. Variation of XIIC

PROCEED IN STEPWISE FASHION →

Figure 2. Stepwise Approach in Studying LSAAP-Type Synthetic Sludge

useful by comparing the soluble form of a chemical contaminant, say $Pb(NO_3)_2$ with the insoluble $Pb(OH)_2$, to distinguish between homogeneous chemical fixation and physical entrapment in an inert matrix. In those instances where true chemical fixation was suggested, attenuated total reflective (ATR) infrared spectroscopy might offer a means of identifying new bond formation indicative of chemical reaction. Whereas ATR could be of value for both inorganic and organic materials, transmission electron microscopy (TEM) would be advantageous for inorganic mixtures where diffraction pattern (crystalline d spacings) changes would be indicative of chemical changes.

4.2.3 Multi-Component Mixtures

Since AAP sludges were generally multi-component heterogeneous mixtures, the studies with binary mixtures would be augmented by incorporating into the mix inert fillers, salts such as $CaSO_4$, additives which would actively participate in the cure (e.g., Portland cement, fly ash), and other representative ingredients. Investigations could also consider other factors including number of components, concentrations, order of addition, processing, and curing conditions. In view of the basic nature of this project, gross effects on the structure and nature of the contaminant-fixative reaction would be sought rather than complete optimization of ingredient composition of the recipes.

4.2.4 Chemical Stability of Formed Bonds

The single, most important property of a successfully E/F-treated sludge was its chemical stability in the ambient (underground) environment. The most direct test of chemical stability was performance under leaching conditions such as those provided by the EPA's Extraction Procedure (EP) which was designated for use in Phase III of this project. The EP test depends, however, upon the physical as well as the chemical properties of the fixed material to the extent that

both affect leaching performance. Important physical properties of a fixed sludge which could impact on its performance in the EP test included bulk density, porosity, permeability and independent factors such as loadings of alkaline material.

The primary purpose of the Phase II basic studies, however, was to investigate the extent and nature of the chemical and/or physical bonds formed during the fixation process and, as such, would be independent of gross physical appearance. Good physical appearance was not indicative of good chemical resistance (to leaching). Hence, it was planned, as part of the Phase II Test Plan, to conduct limited accelerated leaching tests with the binary and multi-component-treated sludge mixtures in order to assess the chemical stability of postulated bonds and structures. Leaching solutions and conditions which were effective for extracting contaminants from untreated and heterogeneous sludge/fixative mixtures would be tested and compared, for example, with chemically-fixed homogeneous E/F-treated sludges. A study of the effect of leaching on the breakdown of chemically fixed structures would be attempted by ATR and/or TEM, if warranted, and if use of these methods proved successful. The methods of choice for leachate analyses were atomic absorption (AA) spectroscopy and infrared (IR) spectroscopy for inorganic and organic species, respectively.

4.2.5 Synthetic Sludges

4.2.5.1 Selection of Candidates

Wastewaters from AAPs and other military installations contained hazardous materials associated with the manufacture and processing of propellants, explosives and pyrotechnics. The toxic pollutants were removed from the wastewaters by a variety of treatment processes prior to release of the waste streams to the environment, in accordance with

47

local and government regulations. The waste materials themselves were concentrated* into sludges or solid residues, both of which were complex heterogeneous mixtures of organic and inorganic origin.

Major sources of hazardous waste sludges from 12 AAPs** were reviewed and characterized in order to develop a basis for synthesizing typical sludges for study on Phase II of this project. Waste types covered the gamut of wastewaters from operations including LAP, Demil, PEP manufacture, initiating explosives, and metal processing. Based on the literature search and the rationale presented in Section 4.0, two categories of synthetic sludges were selected, as shown below:

a. Sludges with Inorganic Toxicants

    (1) Lead*** - Soluble salts: $Pb(NO_3)_2$

                  Insolubles: $PbCl_2$, $Pb(OH)_2$, $PbCO_3$

    (2) Chromium - Cr_2O_3

    (3) Cadmium - $Cd(NO_3)_2$

    (4) Pb/Cr/Cd mixtures

---

*Some sludges such as the LSAAP sludge are extremely dilute (Appendix A)

**Radford, Holston, Iowa, Lone Star, Lake City, Milan, Louisiana, Hawthorne, McAlester, Indiana, Kansas, Crane.

***According to Reference 69 and a telephone conference with Jeri Robinson, Environmental Chemist at LSAAP, the wastewater is treated to desensitize the lead azide by addition of sodium nitrite and nitric acid. Soda ash and lime are added to produce the insoluble hydroxides and carbonates at a pH of 12. Ferric chloride is then added to bring the pH down to about 7 and to flocculate the insoluble heavy metals. Hence, lead may appear in the form of the soluble and insoluble salts shown.

(5) Above with Fillers - Inert (diatomaceous earth)

- $CaSO_4$, $CaCO_3$, $CaCl_2$

- Other additives, e.g., $FeCl_3$

b. **Sludges with Organic Toxicants**

Nitrocellulose (NC) fines

NC plus Fillers - Inert

$CaSO_4$ or $CaCO_3$

Other additives

4.2.5.2 Elimination of Candidates

It is noteworthy that sludges with mixed organic (oils, phenol) and inorganic (metallic) contaminants were excluded deliberately from the plan. Field experience had indicated the desirability of segregating "oil-based" from "water-based" waste effluents prior to placement on the drying beds, thereby avoiding the insurmountable problems associated with mixed sludges.

Also omitted from the plan were:

(a) Labile contaminants such as cyanide and chromate ions, and

(b) Volatile organics (e.g., solvents).

Reasons for omission of labile contaminants, e.g., CN^-, Cr^{+6} from consideration were the relative ease with which these contaminants could be converted to other chemical forms more suitable for further processing. For example, mild oxidation and reduction, respectively,

49

of cyanide to cyanate and Cr^{+6} to Cr^{+3} have been performed successfully in the field prior to immobilization of electroplating chemical wastes. Similarly, volatile organic constituents could be readily removed by further treatment, e.g., distillation, scrubbing, incineration, prior to sludge formation.

Nitrobodies were commonly removed from wastewater by treatments including filtration by diatomaceous earth, or adsorption by granular carbon followed by open burning or incineration. There had been reports of incomplete combustion of the "organic materials" in the residues from open burnings and studies are planned by AEHA to identify the residues chemically.[*] An investigation of the chemical fixation of ash residues from incineration and open burnings would constitute a useful study particularly in view of the increasing interest in combustion as a means for destroying organic contaminants and concentrating hazardous wastes (see Phase IV).

4.2.6 Candidate E/F Systems

The following E/F materials were selected as fixatives for the synthetic sludge mixtures described in the previous section:

    1. Fixatives for Sludges with Inorganic Toxicants

        a. Polysilicates and Mixtures with Lime, Fly Ash
           and Portland Cement
        b. Polysulfides

    2. Fixatives for Sludges with Organic Toxicants

        a. Amine - Cured Epoxides
        b. Polysilicates

This selection was based on an extensive review of the literature and prior experience on the successful adaptation of these materials to

---

[*]Verbal communication, AEHA.

other relevant applications. These materials were particularly desirable for this project for the following reasons:

(1) Contaminants could be molecularly dispersed in the fixatives (with the exception of System 2b with nitrocellulose) and certain mixtures of System 2a.

(2) Chemical and/or hydrogen bonding of the contaminant in the E/F matrix is measurable.

(3) Basic polymerization/curing chemistry of the E/F materials is well understood.

(4) Good mechanical and handling properties of well-cured materials.

(5) Relative ease of processing.

(6) Availability and relatively low cost.

(7) Adaptability to wet (Systems 1a/2b) and dewatered or dry (Systems 1b/2a) sludges.

Polysilicate fixatives cured with lime and mixtures with fly ash and Portland Cement were selected in view of the successful results reported for these systems by LSAAP. Compositions covered the range from simpler homogeneous to more complex heterogeneous systems. Attempts would be made to compare immobilization and resistance to leaching of (a) soluble heavy metal salts molecularly dispersed in homogeneous and homogeneous/heterogeneous matrices with (b) the insoluble heavy metal salts dispersed in these same matrices.

Polysilicate systems could be cured to yield soft-to-hard gels and weak-to-strong rigid solids, depending on the recipe and curing conditions employed. Organic esters had also been reported to produce time-delayed gelation of silicate solutions, presumably by hydrolysis of the ester by alkaline solution.[83] Hence, the interesting possibility existed of reacting polysilicates with nitrocellulose or, more correctly, with cellulose nitrate ester (System 2b).

---

[83]Sodium Silicates, Hydrated and Anhydrous Powders Bulletin, 17-104/478, The PQ Corporation, pp 1-9, 1978.

Metals could be fixed with polysulfides and then cured in mixtures with sulfur by thermoforming means to provide a ductile monolithic matrix structure. Polysulfides were under evaluation as road building materials with promising results.

Epoxides were expected to form solutions with nitrocellulose and thus amine-cured polyepoxides should provide an appropriate matrix for molecular dispersion of the organic contaminants. Hydrogen bonding between matrix and contaminant should occur during consolidation and cure at ambient temperatures. Amine-cured polyepoxides were expected to be stable under leaching conditions, in contrast to the organic-acid-cured material which gave rise to potentially hydrolyzable groups.

4.3. SPECIFIC TEST PLAN

4.3.1 Work Breakdown Structure

The proposed test plan consisted of the following activites.

4.3.1.1 Material Procurement and Characterization

Candidate contaminants and fixative materials would be analyzed, as required, for purity and identification and concentration of other ingredients. Sufficient quantities could be obtained to allow for characterization, experimentation and testing for Phases II and III and for retention for future reference. Sufficient quantities of materials from the same manufacturing lot or batch would be procured to meet the total formulation requirements of the project. In addition, for the polysilicate systems, an attempt would be made to identify and procure material from the same manufacturer (and same lots, if possible) as described in LSAAP, References 68 and 69.

4.3.1.2 Preliminary Processing and Testing

E/F materials would be processed, recipes adjusted, and curing conditions varied until an optimum range of physical characteristics was achieved for each of the candidate baseline (control) systems. This would entail investigation of factors such as concentration of ingredients, order of addition, catalyst level, processing conditions, time, and temperature of cure.

Physical properties of interest at this stage in the test plan included gross homogeneity, degree of cure, freedom from voids and porosity, hardness, viscoelasticity, brittleness, and suitability for inspection by the physical characterization methods proposed.

Conclusions regarding the adequacy of the proposed E/F systems would be drawn and adjustments in recipe made, including gross modifications, if necessary.

4.3.1.3 *Instrumented Characterization Methods*

Specimens prepared during the preliminary processing/testing phase would be examined by the proposed characterization methods, including optical microscopy, infrared spectroscopy, scanning electron microscopy, and the other appropriate techniques described earlier. Interface problems between the instruments and test specimens would be identified and corrected. Other more promising methodologies would be pursued should the earlier choices become unproductive.

4.3.1.4 Tests with Binary Mixtures

Binary mixtures of contaminant and fixative would be cured, tested for gross physical properties (as discussed in 4.2.3, above), and compared with the corresponding baseline system. Observations would be made of the effects of the contaminants on the specimens.

Especially important were properties that affect successful instrumental characterization. Chemical interaction between contaminant and catalyst, for example, would necessitate readjustment of the recipe in order to compensate for this effect and still provide adequate cure and acceptable processing conditions.

Special studies with soluble and insoluble forms of contaminants, e.g., $Pb(NO_3)_2$ versus $Pb(OH)_2$, would be conducted to distinguish between homogeneity and heterogeneity in a controlled system.

Instrumental measurements would stress validation of hypotheses concerning homogeneity, crystallinity, and the nature of the bonding between contaminant and fixative, as discussed previously. This portion of the effort was significant and should lead to a better understanding of the reaction mechanisms involved during chemical fixation of representative AAP sludges.

4.3.1.5 Tests with Multi-Component Mixtures

The purpose of these tests was to determine the effects of representative additives and diluents in synthetic heterogeneous mixes in order to approach more closely the conditions prevalent in typical AAP sludges. Physical appearances, gross properties, and instrumental characterizations would be compared among the three system configurations: baseline versus binary versus multi-component. Data would be analyzed to substantiate or refute hypotheses regarding reaction mechanisms and physico-chemical bonds.

4.3.1.6 Accelerated Leaching

Leaching conditions would be established to enable comparisons to be made between chemically fixed and heterogeneously mixed or physically entrapped contaminants in synthetic sludges. Test results would be compared with conclusions reached by the instrumented

54

characterization studies. Selected baseline, binary and multi-component systems would be included in these tests. Limited formulation changes in sludge compositions could be suggested during these studies only if necessary and if time permitted.

4.3.1.7 Analysis of Data

The data generated during the Phase II laboratory studies was to be analyzed and interpreted. Hypotheses postulated previously and/or developed during the study on reaction mechanisms and microstructure of chemically fixed AAP sludges would be presented. Optimum E/F-treated sludge combinations would be selected for performance characterization assessment in Phase III.

5.0 PHASES II AND III

5.1 BACKGROUND AND OBJECTIVE

The previous sections of this report focused on the rationale for carrying out the project and the test plan for the laboratory studies. The original plan called for completing Phase II, the Bench-Scale Studies, for all candidate sludge-fixative systems prior to initiating Phase III, Product Performance Characteristics Assessment of the more promising systems. It soon became apparent, however, that it was more efficient to proceed from Phase II to Phase III for each candidate fixed sludge system, for it was not possible to judge whether a system was promising from either its physical appearance, gross physical properties, or even its behavior under accelerating leaching conditions. EPA's EP Toxicity Test (40 CFR, Part 261.24) comprised the single test in Phase III which determined the effectiveness of a fixative for stabilizing a sludge. Hence, Phases II and III were carried out sequentially on a system-by-system basis.

This section describes the bench-scale studies which were conducted on two (2) synthetic generic sludges:

    (a) An inorganic sludge, containing heavy metal contaminants, and

    (b) An organic sludge, containing nitrocellulose.

Each of the sludges, in turn, were evaluated in two (2) forms:

        (1) Wet: An aqueous solution - suspension, and

        (2) Dry: A dewatered solution - suspension.

Three types of E/F materials were evaluated as fixatives for the sludges. The candidate fixatives were:

- Polysilicates

- Amine-Cured Epoxides, and

- Polysulfides

The various combinations tested of the two (2) generic sludges, the two (2) sludge forms, the three (3) fixatives and the parameters varied during the study are shown in Table 5. The major toxicants, the other ingredients contained in the synthetic sludges, and the military sludge references are depicted in Table 6.

In order to investigate the nature of the physical/chemical bond created in representative AAP synthetic sludge E/F products, a systematic method of study was followed. The philosophy underlying this approach was to initially carry out tests with relatively "simple" binary mixtures consisting of essentially single contaminants and the fixative materials. For example, binary mixtures of calcium polysilicate with (a) lead, (b) cadmium, and (c) chromium III were examined first. The baseline of data established from these binary mixtures then served as a basis for examining progressively more complex synthetic sludge-E/F products. This approach enabled study of effects due to new and/or changing parameters such as the following: curing conditions; multiple contaminants present (e.g., Cd, Cr and Pb); "inert" filler materials such as $CaSO_4$, diatomaceous earth; additional E/F co-reactants (e.g., polysilicate in combination with Portland cement and fly ash). This method of study offered several advantages: binary mixtures were relatively clean and relatively "simple" for initial work, without excessive oversimplification; the study was focused upon chemical interaction between E/F binder and

57

Table 5

SYNTHETIC SLUDGES SELECTED FOR PHASES II AND III

Sludge Designation	Sludge Type/Form	Major Toxicants in Sludge	Principal E/F Agent	Parameters Varied During Study
A	Inorganic/Wet	Pb, Cr, Cd	Polysilicates: polysilicate and and Portland cement/fly ash	Toxicant Concentrations, presence of inerts and diluents, E/F agents
B	Organic/Dry	NC	Amine-cured epoxide	
C	Inorganic/Dry	Pb, Cr, Cd	Polysulfide	
D	Organic/Wet	NC	Polysilicate	

NOTE: Wet designates aqueous solution - suspension of toxicants.
Dry designates dewatered toxicants.
NC designates nitrocellulose.

58

Table 6.

CANDIDATE SYNTHETIC SLUDGES

"Inorganic" Synthetic Sludges (Types A and C)

Toxicants	Other Ingredients	Military Sludge References
(Heavy Metals)		
Lead: Chloride, Nitrate	Calcium: Sulfate,	
Hydroxide, Carbonate	Carbonate, Chloride	LSAAP Wastewater Treatment
	Oxide	Tobyhanna AD Electroplating
Chromium Nitrate	Iron Chloride	Savanna AD & IAAP Lead Azide*
Calcium Nitrate		

"Organic Synthetic Sludges (Types B and D)

Toxicants	Other Ingredients	Military Sludge References
Nitrocellulose	Calcium: Sulfate	RAAP NG-1/Alcohol Rectification[98]

*Appendix A, Table 7

[98]Wahl, Richard M., Electrolytic Disposal of Lead Azide Sludges in an Acetate-Containing Electrolyte, Mason & Hanger - Silas Mason Co., Inc., Iowa Army Ammunition Plant, Development Department, Middletown, Iowa, January 4, 1982, pp. 35.

toxicants; binary mixtures were suitable for and expedited work with the instrumental characterization methods required in this study; and the data base and methodology could be extended to actual multi-component military wastes stabilized with various fixatives.

5.2 INORGANIC-TYPE SLUDGES TREATED WITH POLYSILICATES, PORTLAND CEMENT AND FLY ASH

Silicate-based mixtures represent one of the largest classes of materials utilized for fixing hazardous wastes. In this study, we have examined the properties and effectiveness of calcium polysilicate, and calcium polysilicate admixed with Portland cement and fly ash, for "chemically" fixing contaminants that are representative of those present in sludges generated by AAPs and other military installations. The purpose of the work was to examine the nature of chemical and physical bonds created in fixing contaminants with calcium polysilicate-based E/F agents, and to measure the effectiveness of the fixation products from an environmental standpoint.

The basis for judging environmental acceptability of products was their performance under EPA's EP Toxicity Test. Characterization of physical and chemical bonds created in E/F products was accomplished by using the following instrumental techniques: scanning electron microscopy (SEM), energy dispersive X-ray (EDX), X-ray diffraction (XRD), and Fourier transform infrared spectroscopy (FTIR). In this section, EP Toxicity Testing and instrumental characterization work are discussed.

5.2.1 Description of Formulation Investigated

Five silicate-based E/F formulae were tested in the laboratory. The principal ingredients of each E/F formula are given in Table 7. Additional details describing weight percentages of each formula ingredient, contaminant fixed, and relevant processing data are provided in Tables 8 and 9.

Formula I represents the least complex E/F combination examined. It consisted of sodium silicate and calcium chloride formulated to fix lead, cadmium, chromium (III) and mixtures of these metals. Solutions of sodium silicate react with polyvalent metals to form precipitates. Such precipitates formed at ambient temperatures and in alkaline media are reported to be "complex mixtures of insoluble metal silicates or hydrated gels with adsorbed metal oxides or metal hydroxides."[73] In the present study, mixtures of calcium chloride and heavy metal(s) [as nitrate(s)] were prepared. Co-precipitation and coagulation of the mixtures were achieved by direct addition of the metal to diluted liquid sodium silicate. Initial work involved co-precipitation of binary mixtures of lead and calcium in the weight ratios shown. Calculations for precipitation were based on the Na_2O content present in the silicate solution and equivalent weights of the calcium and lead compounds. For example, calcium polysilicate (no lead present) was prepared by utilizing sufficient calcium chloride to react with the available Na_2O content (9.1 percent) present in the sodium silicate. Next, polyvalent heavy metals (lead, cadmium and chromium) were introduced with calcium in relative concentrations representative of AAP-type sludges and sufficient Na_2O (sodium silicate) was added to fully co-precipitate all the metals.

---

[73]Roth, Howard; personal communication on January 28, 1983, PQ Corporation, "Silicate Research and Development Department," Lafayette Hill, PA.

61

Table 7

PRINCIPAL INGREDIENTS IN FIVE SILICATE-BASED
E/F FORMULAE UTILIZED IN EXPERIMENTAL WORK

	Formulae				
Principal E/F Ingredients	I	II	III	IV	V
Sodium Silicate	X	X	X	X	X
Portland Cement	0	X	X	0	X
Fly Ash	0	0	X	0	0
$CaCl_2$	X	X	0	X	0
HNO_3	0	0	0	X	X
NaOH	0	0	0	X	X

X = Ingredient present in formula
0 = Ingredient absent

Table 8

"INORGANIC" SLUDGE PLUS POLYSILICATE FIXATIVES WITH SLUDGE
METALS INSOLUBILIZED DURING E/F TREATMENT

Ingredients	Formulae		
	I Parts	II Parts	III Parts
1. Water	44	60	59
2. Sodium Silicate (40 wt %)	44	15	2
3. Portland Cement	--	21	19.5
4. Fly Ash	--	--	19.5
5. Calcium Chloride (20 wt %)	12	4	--
6. Lead[a]	0 to 5	0 to 1	0 to 1
7. Cadmium[a]	0 to 0.02	0 to 0.04	--
8. Chromium[b]	0 to 0.1	0 to 0.2	--
Order of Addition	1+2+(5+6,7,8)	1+(6,7,8)+2+3+5	1+(6)+4+3+2
pH Metals in Sodium Silicate	11.3	11.2	--
pH End of Mix	10.4	11.6	11.7
Cure Cycle	4 days at ambient temp.	3 days at ambient temp.	3 days at ambient temp.

[a]Added as the nitrate salt to water or as a ten percent
solution of the nitrate.

[b]Added as ten percent chromium nitrate.

Table 9

"INORGANIC" SLUDGE PLUS POLYSILICATE FIXATIVES WITH SLUDGE METALS SOLUBILIZED DURING E/F TREATMENT

		Formulae	
	Ingredient	IV Parts	V Parts
1.	Water	55	64
2.	Sodium Silicate (40 wt %)	18	12.5
3.	Portland Cement	--	12.5
4.	Calcium Chloride (24 wt %)	12	--
5.	Nitric Acid (30 %)	11	8
6.	Sodium Hydroxide (10 %)	4	4
7.	Lead[a]	0 to 1	0 to 1
	Order of Addition	1+2+5+(7+4)+6	1+2+5+7+6+3
pH	Metals of Sodium Silicate	1.3	1.3
	End of Mix	8	8.1
	Cure Cycle	4 days at ambient temp.	3 days at ambient temp.

[a]Added as the nitrate salt to water or as a ten percent solution of the nitrate.

Formula II followed the general approach given for Formula I; however, Type I Portland cement was utilized as a co-reactant in equal portions with sodium silicate. Formula III, the most complex E/F agent examined, consisted of Type I Portland cement, fly ash and sodium silicate at about a 20:20:2 weight ratio, respectively.

Formula IV introduced processing variation into the Formula I approach. In these series of experiments, the sodium silicate reagent was first acidified with nitric acid to a pH of about 1.5 to 2. Acidification yielded silicic acid solutions. Silicic acid was blended with soluble heavy metal cations, neutralized and coagulated in a manner similar to that described by Rousseaux (1980)[76] and Rysman de Lockerente (1978).[77] This procedure was completed by co-precipitating the calcium and lead mixtures. Formula V, in turn, followed the approach of Formula IV, but with the addition of Type I Portland cement.

An important distinction between the formulas in Tables 8 and 9 is that under the processing conditions for Formulae I, II and III (Table 8), the heavy metals were presumably fixed as insoluble compounds, as discussed previously. In contrast, in Formulae IV and V (Table 9) a silicious reagent was used to treat the soluble metals prior to coagulation. Formulae I, II and III are representative of the LSAAP sludge-type in which the heavy metals are coagulated as the insoluble precipitates (hydroxides and silicates) in the presence of calcium (I and II) and as the oxide in the presence of fly ash (III),

---

[76]Rousseaux, J.M., Craig, A.B., "Stabilization of Heavy Metal Wastes by the Soliroc Process," PB 81-191900, Proc. on Adv. Poll. Contr. for Metal Fin. Ind., Orlando, FL, April 1980, pp. 70-75.

[77]Rysman de Lockerente, Serge, Van de Voorde, Norbert, "A Procedure for the Treatment of Waste By-Products," Letter of Patent, Report filed in support of, to the International Society of Advertising and Business Assoc./SIPAC, 1978. FR, Brevet D'Invention No. 831.427.

prior to curing. Calcium cations have been reported to promote coagulation of heavy metal precipitates by forming larger size particles. In these systems (I, II, III), the pH is high at the time of addition of the heavy metal nitrates and remains high throughout the mixing and curing cycle.

Systems IV and V were intentionally maintained at low pH, while the heavy metal salts were being added in order to enhance the opportunity for the metals to become chemically bound into a three-dimensional inorganic polymeric network, as some of the literature references suggest or imply[15]. The pH was then raised, presumably, to promote cure of the metal-containing polysilicic prepolymers into high molecular weight, three-dimensional structures.

Portland cement is stated to be capable of forming colloidal metal hydroxides which precipitate in the intersticies of the cement matrix. During the curing process, tubular fibrils form which bind the cement and possibly the metallic precipitates and encase them in the matrix. Claims are also made that the polyvalent metallic cations form ionic cross-links and that Portland cement is hardened and rendered less porous in combination with sodium polysilicates.

The calcium polysilicate-fixed sludges I and IV were extremely hard and glass-like after cure, whereas the cured Systems II, III and V, which contained Portland cement, were crumbly and soil-like.

Test specimens, representative of the various formulations investigated, were photographed. Comments on their physical appearance are summarized below.

---

[3]Conners, J.R., "Ultimate Disposal of Liquid Wastes by Chemical Fixation," 29th Annual Purdue Industrial Waste Conference, Purdue University, West Lafayette, IN, May 7, 1974, p. 906.

The upper and lower surfaces of solidified sodium silicate-calcium chloride-lead nitrate mixtures are different. The amount of lead does not significantly impact the appearance of the solid. Figure 3a shows the top, bottom and side of a 1.3 percent Pb mixture.

(1)   (2)   (3)
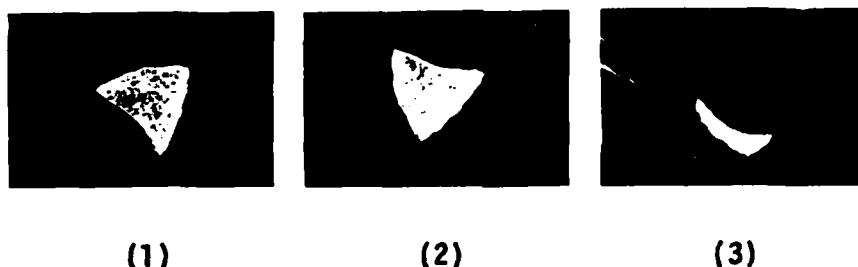
Figure 3a. Top (1), Bottom (2), and Side (3) Views of a Sodium Silicate, Calcium Chloride, Lead Nitrate Mixture (Lead 1.3%)

Figure 3b shows comparable views of a 4.8 percent lead mixture

(1)   (2)   (3)
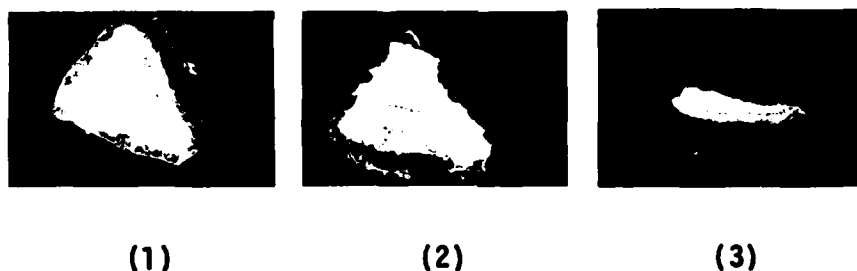
Figure 3b. Top (1), Bottom (2), and Side (3) Views of a Sodium Silicate, Calcium Chloride, Lead Nitrate Mixture (Lead 4.8%).

Sodium silicate alone gives a clear glass-like plastic. For example, see the edge of the sample in Figure 3b.

The addition of fly ash creates a porous, crumbly substance, as can be seen below in Figure 3c(1). The addition of lime to the basic mixture generates an inhomogeneous crumbly material, as shown in Figure 3c(2).

(1)   (2)

Figure 3c. Sodium Silicate, Calcium Chloride, Lead Nitrate
            Mixture Containing (1) Fly Ash and (2) Lime

Portland cement added to the system creates a porous, crumbly material. Additional lead makes the system slightly less crumbly. Figure 3d illustrates this.
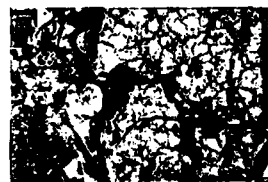
(1)   (2)   (3)

Figure 3d. Sodium Silicate, Calcium Chloride, Lead Nitrate,
Portland Cement Mixtures (1) Lead 0.6%, (2) Lead 1.3%, (3) Lead 4.8%

If a typical sample, such as is shown in Figure 3a, is leached in an Extraction Procedure (EP) test, the result is a white solid that is uniform in appearance. This can be seen below in Figure 3e.

Figure 3e. Water-Leached Sodium Silicate, Calcium Chloride,
Lead Nitrate Sample

5.2.2 Laboratory Procedures

(a) Materials

Sodium Silicate: The principal material utilized in the study was liquid sodium silicate, Grade 40 Clear, vended by Diamond Shamrock Corporation, Soda Products Division, Irving, Texas. Important properties of the reagent are provided below:

Na_2O content	- 9.1%
SiO_2 content	- 29.2%
Total solids	- 38.3%
Wt ratio (SiO_2/Na_2O)	- 3.22
Gravity	- 41.5°Be
Viscosity	- 206 cps

Calcium Chloride: Calcium chloride was utilized as a reactant to precipitate water insoluble metal silicate gel. It was obtained from MCB Manufacturing Chemicals, Inc.

Portland Cement: Type I Portland cement was used in the study. It was obtained from Foreman, Arkansas Cement Corporation, Little Rock Arkansas.

Fly Ash: Fly ash used was a grade obtained from Gifford-Hill Fly Ash Plant at Carson, Texas.

Heavy Metal Salts: Nitrates of chromium were obtained from Mallinckrodt Inc.; nitrates of lead and cadmium were obtained from MCB Manufacturing Chemicals, Inc.

(b)   The laboratory procedures utilized to prepare the polysilicate-fixed synthetic inorganic sludges are described briefly as follows:

   TYPE I   - Each chemical addition was magnetically stirred until the mixture became paste-like. The mixture was then completed by hand stirring and layed out on wax paper under the hood at room temperature to cure. After cure, the material was crumbled and washed through an 0.45- m filter several times.

   TYPE II   - A Waring, variable-speed, two-beater mixer was used to stir after each chemical addition. The material was layed out on wax paper under a hood at room temperature to cure. After cure, the solid was crumbled and washed several times through an 0.45- m filter.

   TYPE III - Same procedure as for Type II, except that the material was layed out on shallow aluminum pan and spread 1/4-inch to 3/8-inch thick to cure.

TYPE IV - Same procedure as for Type III.

TYPE V - Same procedure as for Type III, except that the
mixture became a thick paste and stirring had to be
completed by hand.

5.2.3 EP Toxicity Test Results: Summary and Conclusions

Several accelerated leaching studies were investigated in order
to devise a short-term test (2 to 3 hours) for determining resistance
to leaching of the bonds formed. None of these proved successful in
that they lacked reproducibility and did not correlate well with the
EPA standard EP Toxicity Test. However, these studies were useful in
that they provided data which suggested that:

(1) The "chemical" fixation of heavy metal contaminants by
calcium polysilicate, as postulated in the literature, may
be an artifact, or

(2) The "bonds" formed during fixation are either physical in
nature or are very weak.

These preliminary studies led to a decision to proceed with the
Phase III standardized EP Toxicity Test, in accordance with 40 CFR,
Part 261.24, in order to better characterize the nature of the chemical
fixation process.

Table 10 summarizes the EP Toxicity Test results for a series of
batches of synthetic fixed sludges containing varying concentrations of
lead nitrate and mixtures of lead, cadmium and chromium nitrates in a
Type I calcium polysilicate system. The relative percentages of metals
were similar to those found in AAP-type sludges where calcium

Table 10

EP TOXICITY SUMMARY - CALCIUM SILICATE SYSTEM I

	Metal Content in Fixed Sludge*		Total Metal Available in EP Toxicity Test***	EP Toxicity Test Summary		Metal Extracted From EP-Toxicity Test Specimen
	%	PPM	PPM	PPM	Final pH	%
Lead**	0.02	200[1]	10	2.3;1.8	10.8	23;18
	0.04	400	20	4.7	10.7	23.5
	0.05	500[2]	25	4.3	10.7	17
	0.655	6,550	328	20.6	10.8	6.2
	1.3	13,000	650	18.0	10.8	2.8
	2.54	25,400	1270	19.4	10.7	1.5
	4.88	48,800	2440	33.0	10.7	1.4
Cadmium**	0.005	50[1]	2.5	0.48	10.6	19.2
	0.01	100[2]	5	0.58	10.7	11.6
Chromium**	0.027	270[1]	13.5	1.2	10.6	8.9
	0.053	530[2]	26.5	2.8	10.7	10.6

*Cured and dried.

**Maximum allowable concentrations in EP Toxicity Test are 5/1/5 ppm, respectively, for Pb/Cd/Cr.

***100-gm test specimen in 2-liters final volume.

[1,2]Same batch contains three metals at ppm's shown.

polysilicate is used to fix three metals, Pb^{+2}, Cd^{+2}, Cr^{+3} in concentrations of 200:50:270 and 500:100:530 ppm.[68] It may be seen that, in general, the concentration of metal in the leachate increased with rising metal content in the fixed sludge. The pH of the leachate remained high (~10.5) even after addition of the maximum 400-mL of 0.5 N acetic acid per 100-gram test specimen, in accordance with the protocol for the EP Toxicity Test.

Calcium polysilicate acts rapidly to neutralize the acetic acid leaching solution to produce final solution pHs of 10.7 to 10.8. Another observation is the apparent inverse relation between quantity of contaminant fixed and weight percent of contaminant leached. Thus, the percent of metal (lead and cadmium) extracted from the test specimens appeared to be greater at the lower concentrations of contaminant in the fixed sludge.

As discussed subsequently, the alkalinity and buffering actions are thought to impart a beneficial effect on contaminant stability under acid leaching in a manner similar to that proposed by Anderson (1982).[3]

The data from Table 10 are plotted in Figure 4 as Metal Concentration in the Mix Versus the Corresponding EP Toxicity Test Values. Also shown are the EPA maximum allowable concentrations for each of the three metals in the leachate. It is noteworthy that the rate of rise of metal content in the leachate is greater at the lower levels of contaminant in the mix (0 to 10,000 ppm) than at the higher levels (10,000 to 50,000 ppm) of contaminant.

---

[68]Robinson, Jeri, "Chemical Fixation of Sludge," Lone Star Army Ammunition Plant, no date, 32 pp.

[3]Anderson, Marc A., Robert K. Ham, Ranier Stegmann, Robert Stanforth, Robert Pojasek, ed., Toxic and Hazardous Disposal, Volume 2, Ann Arbor Science, 1982, pp. 145-168.
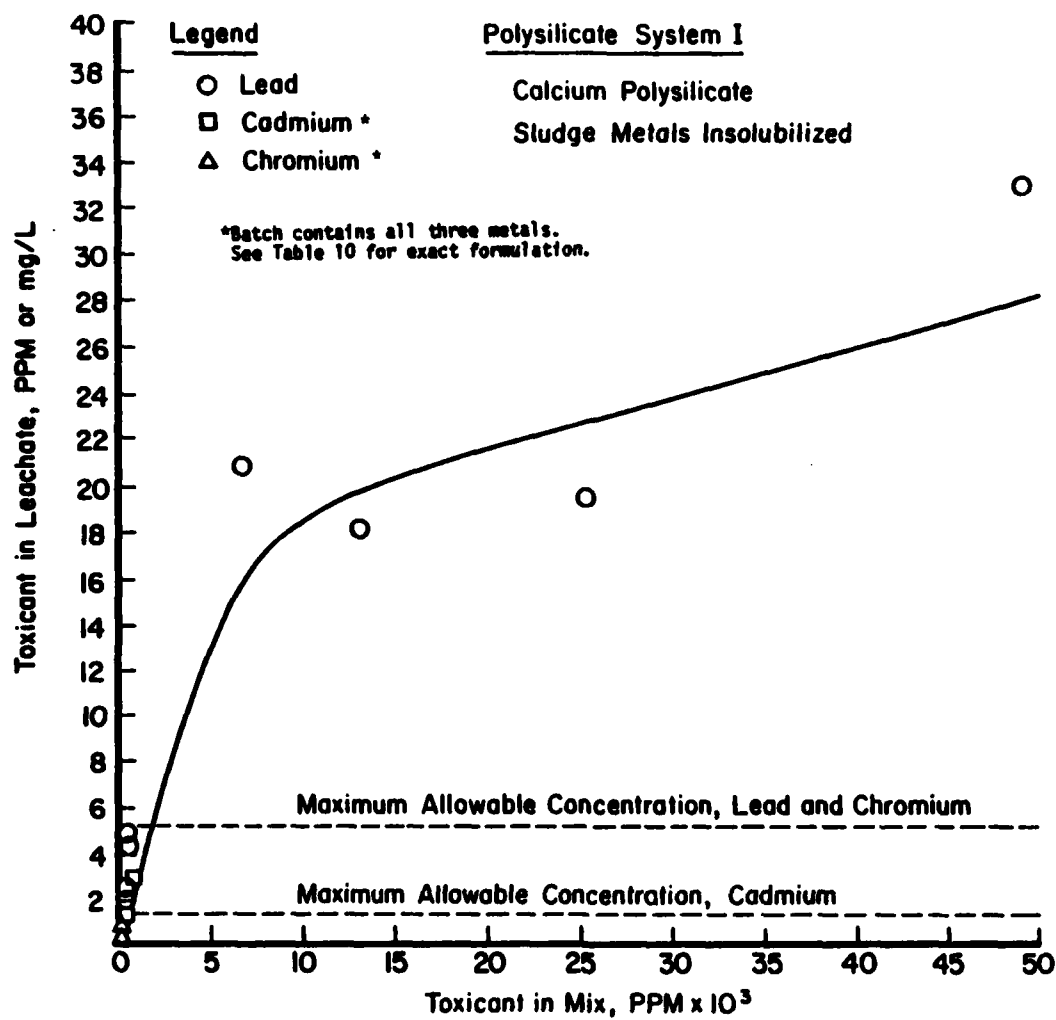
Figure 4. Metal Concentration in Leachate Versus
Concentration of Metal in Mixture

74

One might expect a curve of this shape given the following conditions:

- Insoluble precipitates with low, constant equilibrium solubility products.

- Constant specimen weight (100 gm).

- Constant volume of 0.5 N acetic acid (400 cc).

- Constant volume of leachate (2 liters).

These results suggest that:

(1) The apparent chemical fixation of heavy metals by calcium polysilicates in a highly alkaline media may be an artifact,

(2) The EP Toxicity Test results merely represent a partial neutralization of alkali by the acetic acid in a highly buffered alkaline medium, resulting in a partial dissolution of the metals in accordance with the low, constant solubility products of the insoluble metal precipitates,[78] and

(3) The addition of materials more alkaline than sodium silicate should show improved (lower) EP Toxicity Test results.

Table 11 presents the EP Toxicity Test results for a series of batches containing heavy metal contaminants, sodium silicate, Portland cement, and (in one case) fly ash; namely, Systems II, III and V.

As noted previously, high alkalinity plays an essential role in neutralizing acidic leaching solutions. The high alkalinity, or acid neutralizing capacity, of Portland cement and fly ash maintains the high pH required to resist extraction of acid soluble metals. Again, the data in the last column show an inverse relationship in percent

---

[78]Salas, Robert K., Robert B. Pojasek, ed., Toxic and Hazardous Waste Disposal, Vol. I, Ann Arbor Science, 1929, pp. 321-348.

Table 11

EP TOXICITY TEST SUMMARY
POLYSILICATE SYSTEMS CONTAINING PORTLAND CEMENT

	System	Metal Content in Fixed Sludge*	Total Metal Available in EP Toxicity Test ***	EP Toxicity Test Summary		Metal Extracted From EP-Toxicity Test Specimen
		PPM	PPM	PPM	Final pH	%
Lead**	II	500	25	<0.5	10.3	< 2
		900	45	<0.5	10.4	< 1
		1,200	60	<0.5	10.3	< 0.8
		24,000[1]	1,200	<0.5	10.9	< 0.04
	III	1,130	57	<0.5	10.6	< 0.87
		11,400	570	<0.5	10.7	< 0.09
	V	688	34	<0.5	9.6	<1.5
		6,783	339	<0.5	9.9	<0.15
Cadmium**	II	240[1]	12	<0.01	10.3	<0.08
Chromium**	II	1,040[1]	52	0.4	10.3	0.8

*Cured and dried.

**Maximum allowable concentrations in EP Toxicity Test are 5/1/5 ppm, respectively, for Pb/Cd/Cr.

***100-gm Test specimen in 2-liters final volume.

[1]Same batch contains the three metals at ppm's shown.

metal extracted with increasing metal content in the EP Toxicity specimen -- as was the case with the calcium polysilicate-fixed sludge (System I).

Also noteworthy are the comparable data obtained with sludges in which the metals are either solubilized (Systems IV, V) or insolubilized (Systems I, II, III) prior to curing. These results conform to the previous suggestion that we may be dealing with insoluble metal hydroxides (and other insoluble metal compounds) in a highly alkaline-buffered medium rather than with chemical fixation of the metals in an inorganic polymer matrix. In other words, these results demonstrate that polysilicates formed by fixing metals from either acidic or basic media are essentially equivalent in terms of their inherent resistance to acetic acid leachability. "Chemical" fixation of the pre-solubilized metals into an inorganic polymer matrix via acidification of E/F agents, if occurring, may play only a minor role at contaminant-to-silicate ratios and conditions studied here.

Data reported by Day and Zimmerman for sludges of the type shown in Table 11 and fixed with cementitious materials are in line with our findings. Moreover, the ingredients utilized in our study came from the same lots used in their work.* For example, two successful fixed sludges reported by Day and Zimmerman include the following:

---

*Ms. Jeri Robinson, Day and Zimmerman kindly supplied us with 5- to 10-lb retainer samples of sodium silicate, Portland Cement Type I, fly ash and lime taken from the same lots previously used at LSAAP with successful results.

77

Sludge	Portland Cement	Sodium Silicate	Lime	Fly Ash	Lead Content in Fixed Sludge	EP Toxicity Test Results	Lead Content in EP Tox Test Specimens		Percent Extracted From Specimens
Parts	Parts	Parts	Parts	Parts	PPM*	PPM	pH	PPM	%
300	100	70	--	--	400-1400	0.27	10.4	20-70	0.1-1.4
300	--	--	50	200	340-730	0.34	11.2	17-37	0.9-2.0

*Range shown because of unknown moisture losses during cure.

Since the Day and Zimmerman data are for low-metal-to-fixative levels only, the correlation of their data with that of Figure 4 would show points very close to the origin. Consequently, they are not plotted.

Figure 5 is a plot of Quantity of Contaminant in the Leachate (subsequent to performing the EP Toxicity Test) Versus Quantity of Contaminant in the original cured mix for systems containing Portland cement. The previous curve for the calcium polysilicate-fixed sludges is also shown for comparison on the same graph.

It would appear from these curves that highly alkaline Portland cement (and fly ash) consume or neutralize the acetic acid leaching solution employed in the EP Toxicity Test, thereby preventing dissolution of the insoluble metal precipitates. The effectiveness of this is demonstrated by the low concentrations listed in Table 11 and the horizontal constant, low measured levels of contaminants shown in Figure 5. This enhancement of leaching behavior was demonstrated for lead levels up to 24,000 ppm in the fixed-sludge product.

Polysilicate/Portland Cement/Fly Ash Systems

Portland Cement Absent

Contaminant in Leachate, PPM or mg/L

28 26 24 22 20 18 16 14 12 10 8 6 4 2

(Cd) (Cr)

Contaminant in Cured Mix, PPM x 10³

5 10 15 20 25 30 35 40 45 50

System*		Contains Lead	Contains Chromium & Cadmium	Contains Fly Ash	Sludge Metals Insolubilized	Sludge Metals Solubilized
I	○	✔			✔	
II	◇	✔	✔		✔	
III	□	✔		✔	✔	
IV	△	✔		✔		✔

*See Table 11 for exact formulation.

Figure 5. Contaminant in Leachate, ppm Versus Contaminant in Cured Mix

79

If fixation of heavy metal contaminants by polysilicate/Portland cement/fly ash is a consequence of the insolubility of the metal hydroxides and other metallic compounds with low solubility products in a highly alkaline-buffered media, and chemical reactions of the heavy metals via ionic or covalent bonding into a three-dimensional inorganic network does <u>not</u> occur, then it should be possible to demonstrate the following:

> Mixtures of the synthetic sludge containing the metallic contaminants and fixative, <u>equally fortified with buffered, highly alkaline ingredients but uncured, should also show low solubility of the contaminants in the leachate</u> subsequent to the EP Toxicity Tests.

Table 12 confirms the successful "fixation" of lead in uncured sodium silicate/Portland cement mixtures (System II). The greater alkalinity of the Portland cement system compared to calcium polysilicate was demonstrated by titrating the individual materials with acid. The comparative titration data for Portland cement, sodium silicate, and mixtures of the two are shown in Table 13. The last column, mL 1.0 N HCl/gm ingredient may be compared, qualitatively, with the 4 mL 0.5 N acetic acid/gm used in the EP Toxicity Tests. Ignoring differences in buffering action and the effects of other additives, Portland cement, nevertheless, is seen to be capable of absorbing seven times as much acid as sodium silicate. This is in agreement with our observations on the comparative effectiveness in the EP Toxicity Test of E/F systems containing these ingredients.

In summary, the EP Toxicity Test results for inorganic-type sludges treated with polysilicates, Portland cement and fly ash show that (1) fixation of heavy metal contaminants by these fixatives is a consequence of the use of highly alkaline buffered media and that (2) chemical reactions which incorporate the metals into a

Table 12

EFFECT OF PORTLAND CEMENT AND CURE

Portland Cement	Metal Content In Fixed Sludge	EP Toxicity Test Results			
		Uncured		Cured*	
	PPM	PPM	Final pH	PPM	Final pH
PRESENT	3,600	0.5	10.9	0.5 to 0.5	9.7 to 11.6
	34,800	0.5	11.1	0.5 to 0.5	10.8 to 11.6
ABSENT	1,000	1.4	10.6	3.2 to 4.7	10.4
	10,000	20	10.7	18 to 24	10.4

*Data from concurrent and previously cured batches.

Table 13

ACID REQUIRED TO NEUTRALIZE

Ingredient	pH		mL HCl**/g Ingredient
	Initial	Final	
PORTLAND CEMENT	12.3	3.6	22
SODIUM SILICATE	11.6	1.7	3
(50) PORTLAND CEMENT (50) SODIUM SILICATE	11.9	3.1	13

**1.0 N
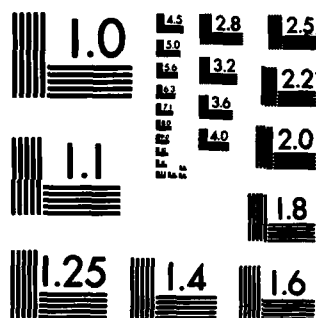
MICROCOPY RESOLUTION TEST CHART

NATIONAL BUREAU OF STANDARDS-1963-A

three-dimensional inorganic network[15] may not be the primary criteria to effect contaminant leaching stability.

5.2.4 Instrumental Characterization of Polysilicate-Fixed Synthetic Sludges Containing Heavy Metals

A number of analytical tools were investigated for the purpose of acquiring physical data which could be used to either identify new structures or changes in structure attributable to chemical fixation. These include, as mentioned earlier, infrared spectroscopy (IR), scanning electron microscopy (SEM), energy dispersive X-rays (EDX), and X-ray diffraction (XRD) measurements. In some cases, measurements were made before and after leaching by the EP Toxicity Test.

5.2.4.1 Instrumental Procedure

Infrared spectra were obtained on a Digilab FTS-15C Fourier Transform Infrared (FTIR) Spectrometer. The instrument was used to study the sodium silicate fixed inorganic mixtures.

The Scanning Electron Microscopy (SEM) and EDX measurements were made on a Cameca-Microbeam equipped with a Kevex energy dispersive X-ray unit. The X-ray diffraction results were obtained using a Nonius Guinier camera with CuK source.

Sample Preparation:

The IR samples examined with the FTIR were prepared by mixing a small amount of the sample (1-5%) with potassium bromide using an agate mortar and pestle. The resulting mixture was pelletized in a pellet

---

[15]Connors, J.R., "Ultimate Disposal of Liquid Wastes by Chemical Fixation," 29th Annual Purdue Industrial Waste Conference, Purdue University, West Lafayette, IN, May 7, 1974, p. 906.

press before the spectra were obtained. The nitrocellulose samples were also studied as KBr pellets, but other samples were mixed with nujol or fluorolube, two mineral oil-type components, to see if certain interferences could be eliminated.

The SEM samples were coated with carbon or carbon followed by gold, depending on the information to be obtained. Coating was accomplished by sputtering. The carbon-only samples were used for the energy dispersive X-ray studies.

Samples analyzed by X-ray diffraction were first ground then mixed with mineral oil and applied to a 1/4-mil mylar film support. The signal is focused by a curved quartz crystal and recorded on Kodirex film.

5.2.4.2 Infrared Spectroscopy

Figures 6a and 6b are transmittance spectra for, respectively, (a) a mixture of sodium silicate and calcium chloride, and (b) this same mixture to which 4.5 weight percent of lead nitrate was added. Comparison of the two figures shows no significant shifts to occur in any peak positions as a consequence of adding $Pb(NO_3)_2$. Moreover, no new peaks are observed except for NO_3^-, nor do the peak intensities appear to significantly change.

The conclusion reached is that no significant lead-silicate compound formation is observable by IR. Evidence of lead-chloride compound formation was not obtained. Lead chloride is not a good fixation candidate in that it exhibits partial water solubility. Therefore, no attempt was made to extend the lower working range of the IR.

83
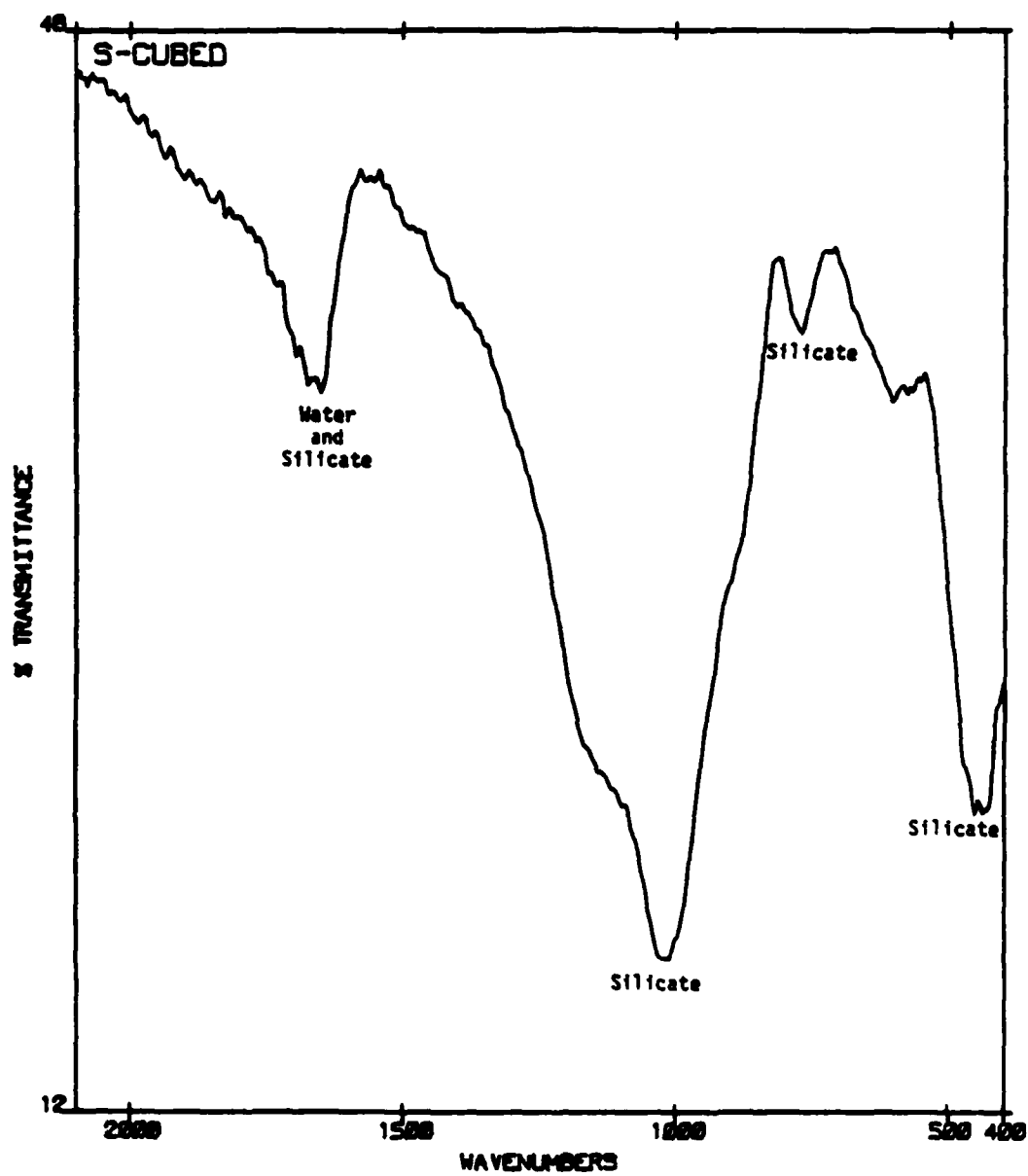
Figure 6a.   Infrared Spectrum of Sodium Silicate and Calcium Chloride
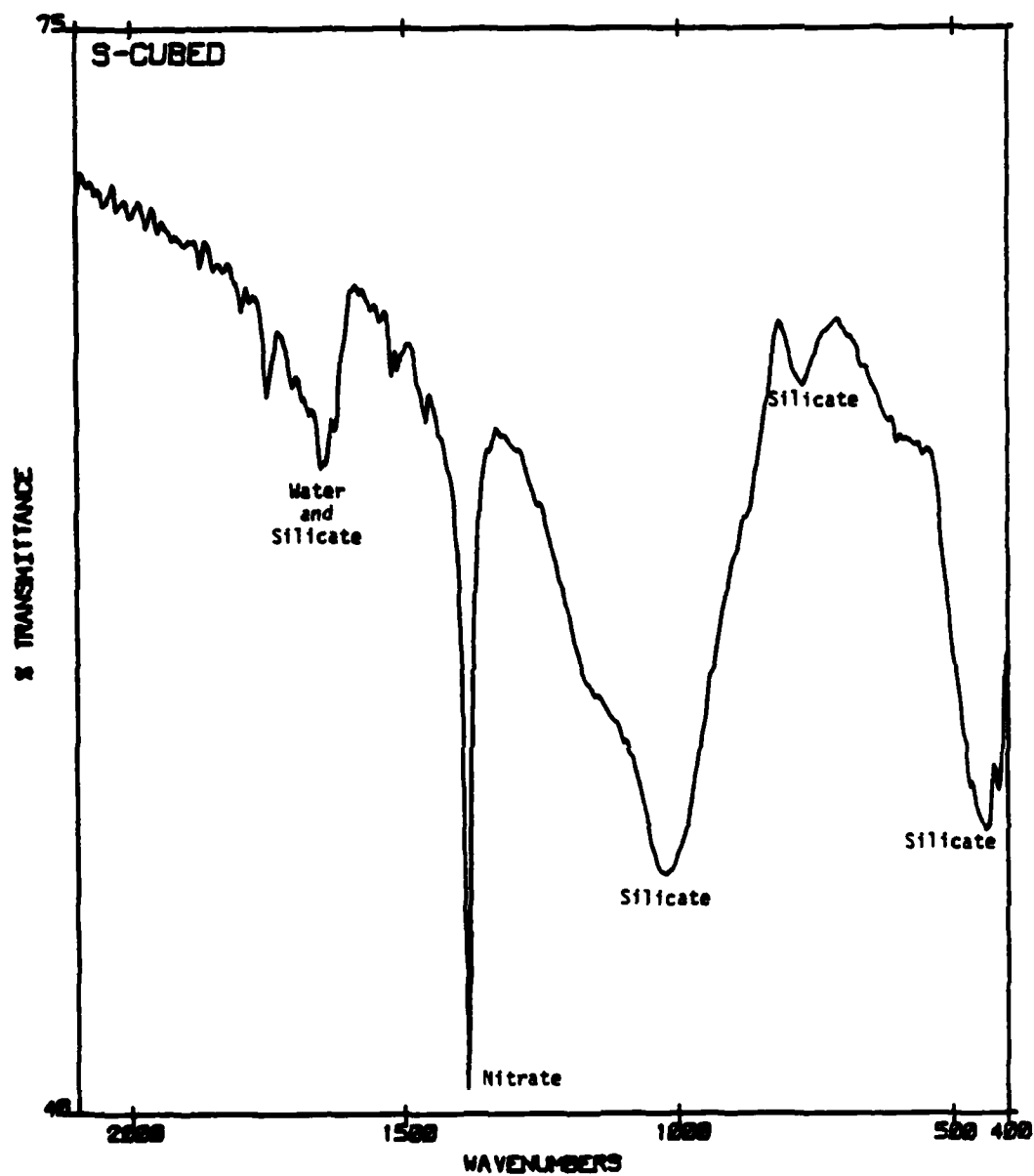
Figure 6b.   Infrared Spectrum of Sodium Silicate,
Calcium Chloride and Lead Nitrate (4.5%)

5.2.4.3 Scanning Electron Microscopy and Energy Dispersive X-Ray Studies

The sodium silicate/calcium chloride/lead nitrate (4.5 weight percent) mixture described above was examined by EDX "before" (Sample A) and "after" (Sample B) leaching using a CAMECA-Microbeam instrument. The results are shown in Figures 6c and 6d, respectively. SEM/EDS maps of lead, calcium and silicon, and a SEM photomicrograph of the material are shown in Figure 6e. The results of these studies may be summarized as follows:

(1) Pre-leach Material (Sample A)

    (a) The sample is present in two layers: smooth glass top and rough crystalline bottom.

    (b) No lead is evident in the top, bottom or interior.

    (c) Cubic crystals observed on the bottom material are presumably NaCl.

(2) Post-Leach Material (Sample B)

    (a) The sample presents a uniform white appearance.

    (b) Lead is present and is uniformly distributed.

    (c) The other elements are also uniformly distributed.

The conclusions reached for these studies are:

(1) Lead in the pre-leach material is probably uniformly distributed, but is too dilute to see in the surface layer. There is no preferential association of lead with any other element. There are no inhomogeneities in the system.

(2) Leaching removes NaCl and silicate glass exposing the lead. Lead is not associated with any other element.

CAMECA-MICROBEAM
04-MAY-83

K 2-14 BI

PR- 20S   20SEC   0 INT
V-8162 H-10KEV 1:10 A6-10KEV 10

S-CUBED
SAMPLE A
N45 600
15. KV
5 NA

7168
6144
5120
4096
3072
2048
1024

< O.OOKEV   XES   1O.24KEV>

0.00   1.28   2.56   3.82   5.12   6.40   7.76   9.04

Sodium
Silicon
Chlorine
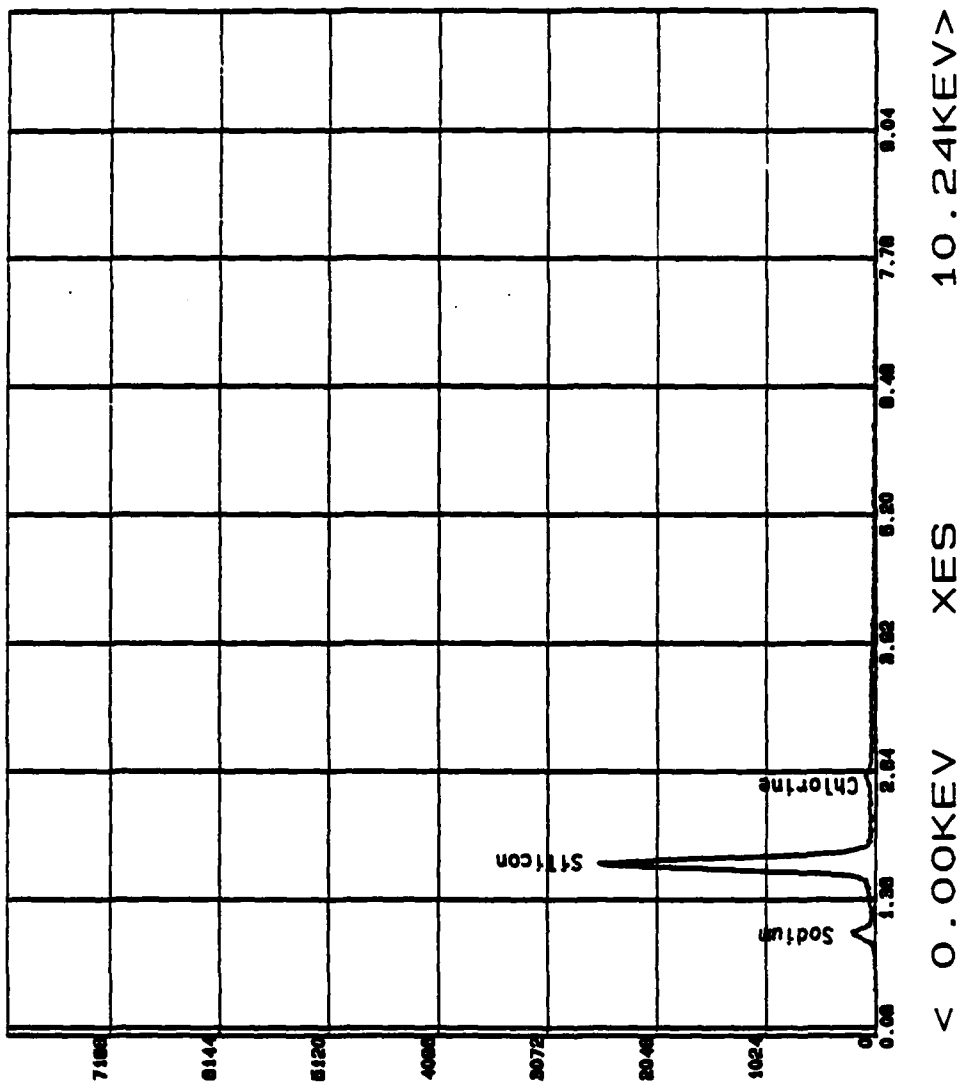
Figure 6c.   Energy Dispersive X-Ray Trace of 4.5% Lead Mixture Pre-Leaching

87

CAMECA-MICROBEAM
04-MAY-83

K Z-14 BI   0 INT

RA- 20S   20SEC
V-8192 H-10KEV 1:10 A0-10KEV 10

S-CLRED
SAMPLE B
BEAM SCAN
MAG 800
15, KV
5 MA

Sodium   Silicon   Lead   Calcium

< 0.00KEV   XES   10.24KEV>
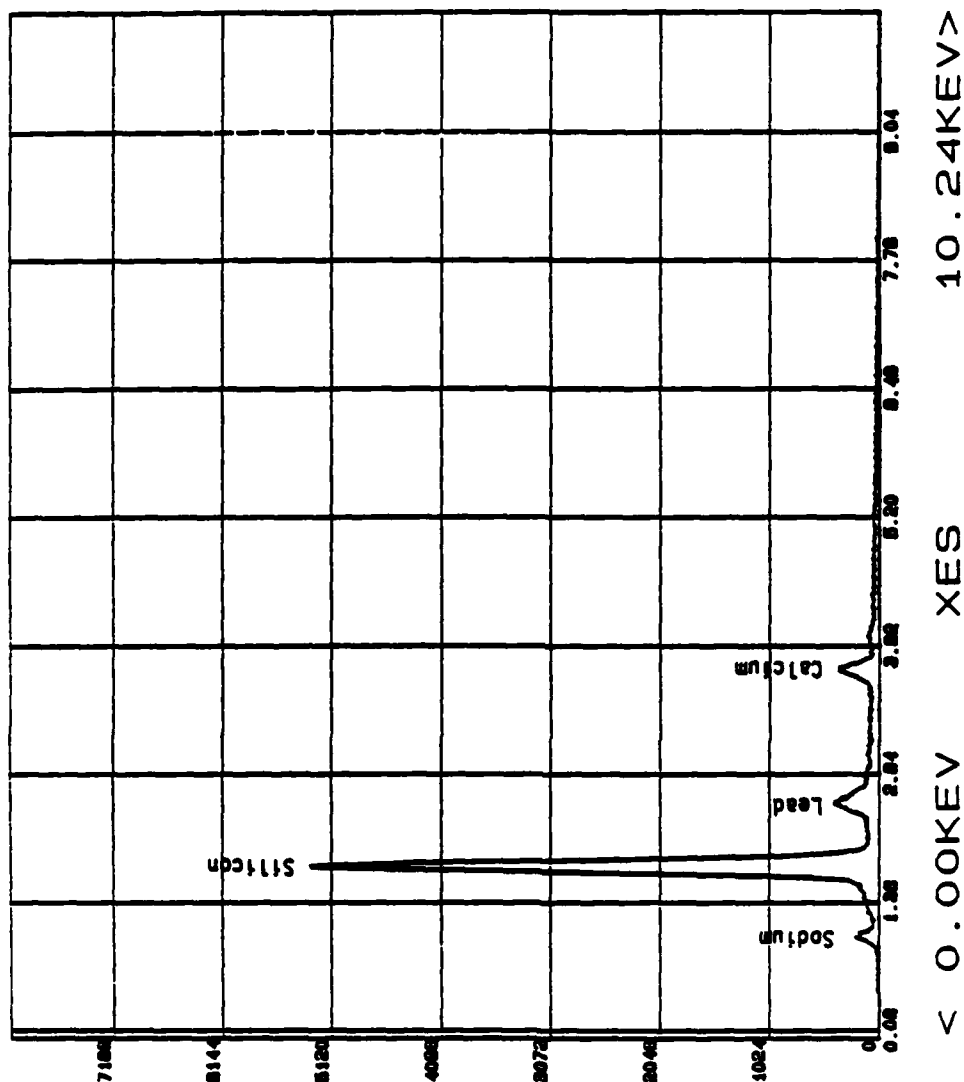
Figure 6d.   Energy Dispersive X-Ray Trace of 4.5% Lead Mixture Post-Leaching
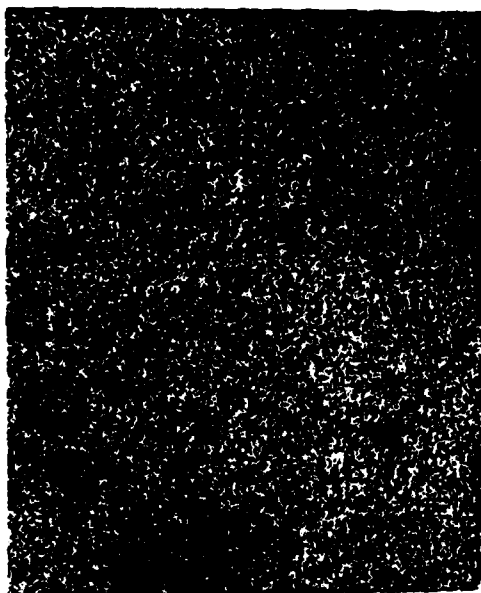
SEM/EDX MAP
OF LEAD (400X)

SEM PHOTOMICROGRAPH
(BACK SCATTERED ELECTRON) 400X
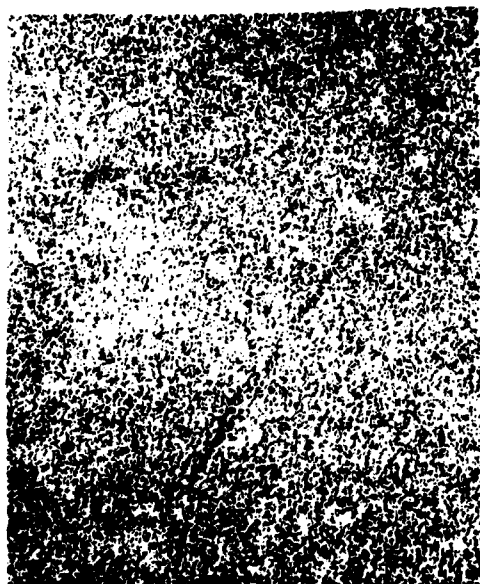
SEM/EDX MAP
OF CALCIUM (400X)

SEM/EDX MAP
OF SILICON (400X)

Figure 6e. SEM Photomicrograph and SEM/EDX Maps of Sodium
Silicate/Calcium Chloride/Lead Nitrate (5 wt%) Mixture

5.2.4.4 X-Ray Diffraction Studies

Examination of the same $Na_2SiO_3/CaCl_2/Pb(NO_3)_2$ system described above by X-ray diffraction showed the following results:

(1) Neither the pre- nor the post-leaching samples contained crystalline lead compounds ($PbNO_3$, $PbCl_2$ or $PbSiO_3$).

(2) The pre-leached sample contained considerable NaCl.

(3) The post-leached sample contained no crystalline compound.

from which it was concluded that

(1) No crystalline compounds are present.

(2) Lead is not associated with NO_3^- or Cl^- and therefore is probably present as a silicate or hydroxide.

(3) All silicate compounds, including any lead silicate, are amorphous.

5.2.4.5 Physical Measurements: Summary and Conclusions

In summary, IR, SEM, EDX, and X-ray diffraction measurements of calcium polysilicate-treated AAP sludges containing lead nitrate did not reveal significant formation of new compounds or crystalline structures indicative of chemical fixation.

These results support the EP Toxicity Test results discussed in the previous section; namely, that the heavy metals presumably are not incorporated tightly by chemical bonds into a three-dimensional inorganic polymeric or polycrystalline network.

5.3 CHEMICAL FIXATION OF NITROCELLULOSE (NC) WITH
(a) POLYSILICATES AND (b) AMINE-CURED EPOXIDES

5.3.1 Fixation of NC with Polysilicates

Organic esters have been reported to produce time-delayed gelation of silicate solutions (Diamond Shamrock Technical Bulletin).[10] The interesting possibility existed, therefore, of reacting polysilicates with nitrocellulose or, more correctly, cellulose nitrate ester. The possible use of a common fixative for both inorganic (heavy metals) and organic (NC) sludges was also of interest.

Prior to undertaking these studies, however, it became necessary to obtain or develop a suitable analytical procedure for NC since the quantity of NC in the EP Toxicity Test leachate would determine the effectiveness of fixation. The same polysilicate binders described in the previous section were utilized in these studies. Two grades of NC were investigated (a) Hercules Smokeless Powder Type A[87] and (b) NC fines produced at Radford Army Ammunition Plant. Both of these grades were shipped to S-CUBED under approximately 50 percent water in conformance with the regulations for shipping a flammable solid.

5.3.1.1 Safety Tests

An in-house safety program was established to ensure operational safety during formulation, cure and testing of mixtures containing NC. Impact sensitivities and sympathetic detonation tests were carried out on NC and mixtures of NC with sand, polysilicates and epoxy binders.

---

[10]Brochure on Chemical and Physical Properties of Nitrocellulose, Hercules, Inc., Wilmington, Delaware.

[87]Technical Bulletin SP-LS-7, Grades of Liquid Sodium Silicates, Diamond Shamrock Corporation, 1981.

The latter testing was conducted at S-CUBED's Green Farm Facility at Miramar Naval Air Station, which is close to the S-CUBED laboratories. As a consequence of the safety program, the shielding in our laboratory hoods was modified to withstand detonation of several grams of C-2 and the laboratory batch size for mixtures containing dry NC was limited to the same quantity.

A drop test fixture for investigating impact sensitivities of NC mixtures was fashioned after the Bureau of Mines tester. In this test, a 2-Kg weight is dropped onto the test specimen (approximately 20 mg) contained in a circular shallow cavity on an unhardened steel block.

Using this device, positive detonations were obtained with desensitized PETN controls and dry NC. The latter was well within the low drop height range reported by Picatinny Arsenal and Bureau of Mines testers. However, wet NC, three dried NC-cementitious mixtures (Batches 513A, 513B and 513C in Table No. 5), and one dried NC-epoxy mixture failed to detonate on impact.

In addition, experiments were carried out to determine the relative sensitivity to explosive impacts of up to 200 kilobars of the same dried NC-cementitious mixtures cited above and an inert control. In no case did the aluminum sheet indicator plates used in this test provide evidence that the explosive reaction propagated beyond the end of the C-2 charge.

Tests of two epoxy-fixed sludges containing nine weight percent NC fines were negative when exposed to 200 kilobars of explosive impact. However, wet NC and 50:50 mixtures of wet NC:Wet sand controls showed some evidence of a partial sympathetic propagation of the explosion in the region of the test material. Both Hercules NC and RAAP NC Fines behaved similarly in the control tests with wet sand. Wet NC-sand mixes were negative on impact sensitivity testing, however.

92

The safety studies, although incomplete, confirmed that dried NC is less stable than the wet material and that it can be made to detonate. The wet NC in the presence of gritty solids such as sand, however, can be made to undergo sympathetic detonation in the presence of an exploding charge of composition C-2.

Subsequent to these tests, experimental mixes containing dry NC were limited to a few grams behind suitable safety shielding. Batches up to 100 grams in size (sufficient to conduct the EP Toxicity Test), and containing up to 15 weight percent (on a dry basis) NC wetted with 55 weight percent water, were prepared in the laboratory. Care was taken during mixing to control any exotherm which might result from dissolution of NC in DETA by slow addition and cooling, if necessary. Also, gritty solid additives were not used in the recipe.

5.3.1.2 Analytical Procedures for NC Determination

An infrared adsorption procedure for determining nitrocellulose in solid propellant (MIL Std)[54] was evaluated with aqueous extracts of NC. The characteristic peaks recommended for NC are 1275 cm^{-1} (strong peak) and 1650 cm^{-1}.[2] Test results using this procedure were unsatisfactory, however. Hence, the method was abandoned in favor of a colorimetric procedure (EPA, 1979)[31] which proved satisfactory.

The colorimetric procedure, which depends on the determination of nitrite, is described briefly below:

---

[54]Military Standard Method T209.10, 1 Sept. 1980.

[2]Anal. Chem, 32 (4) 495 (1960).

[51]Method 353.2, EPA-600/4-79-020, 1979.

A series of controls were prepared which included a blank, three standard sodium nitrate solutions representing 0.2; 0.6; and 1.0 mg/L, two filtered spikes, and two unfiltered spikes. These controls and the samples to be tested all underwent the following preparation for the absorbance tests:

A sample measuring 2 mL was poured into a test tube and 1 mL of 5 N sodium hydroxide was added and thoroughly mixed. The test tube was placed in a 70° C water bath for 10 minutes, removed, and allowed to cool to room temperature. Four (4) mL of 0.03 M sulfuric acid was mixed thoroughly in the sample solution and the entire solution allowed to stand for 10 minutes. Then 1 mL of N (1-naphthyl) ethylenediamine (NED) was mixed in and allowed to stand for 15 minutes. The sample was then ready for testing on a Bausch and Lomb Spectronic 20 IR Spectrophotometer using a wavelength of 520 nm. A blank consisting of nitrate-free water and the prepared standard nitrate solutions was used to prepare a calibration curve. The spiked data were utilized to plot the curve in order to ensure test integrity. The calibration curve used in the study is illustrated in Figure 7.

5.3.1.3 Laboratory Procedures

Radford AAP NC fines and Hercules Smokeless Powder Type A were each admixed with polysilicate and polysilicate/Portland cement fixatives. Controls containing celite (diatomaceous earth) and calcium carbonate were also prepared. The compositions of the fixative/NC sludge mixtures are shown in Table 14.

The general procedures for preparing the batches were as follows:

The 503 series of mixes was prepared by weighing each chemical separately and then putting them into a 2-L nalgene bottle containing 1600 mL of nitrate-free water. These samples were then tested by the EP Toxicity Test procedures.
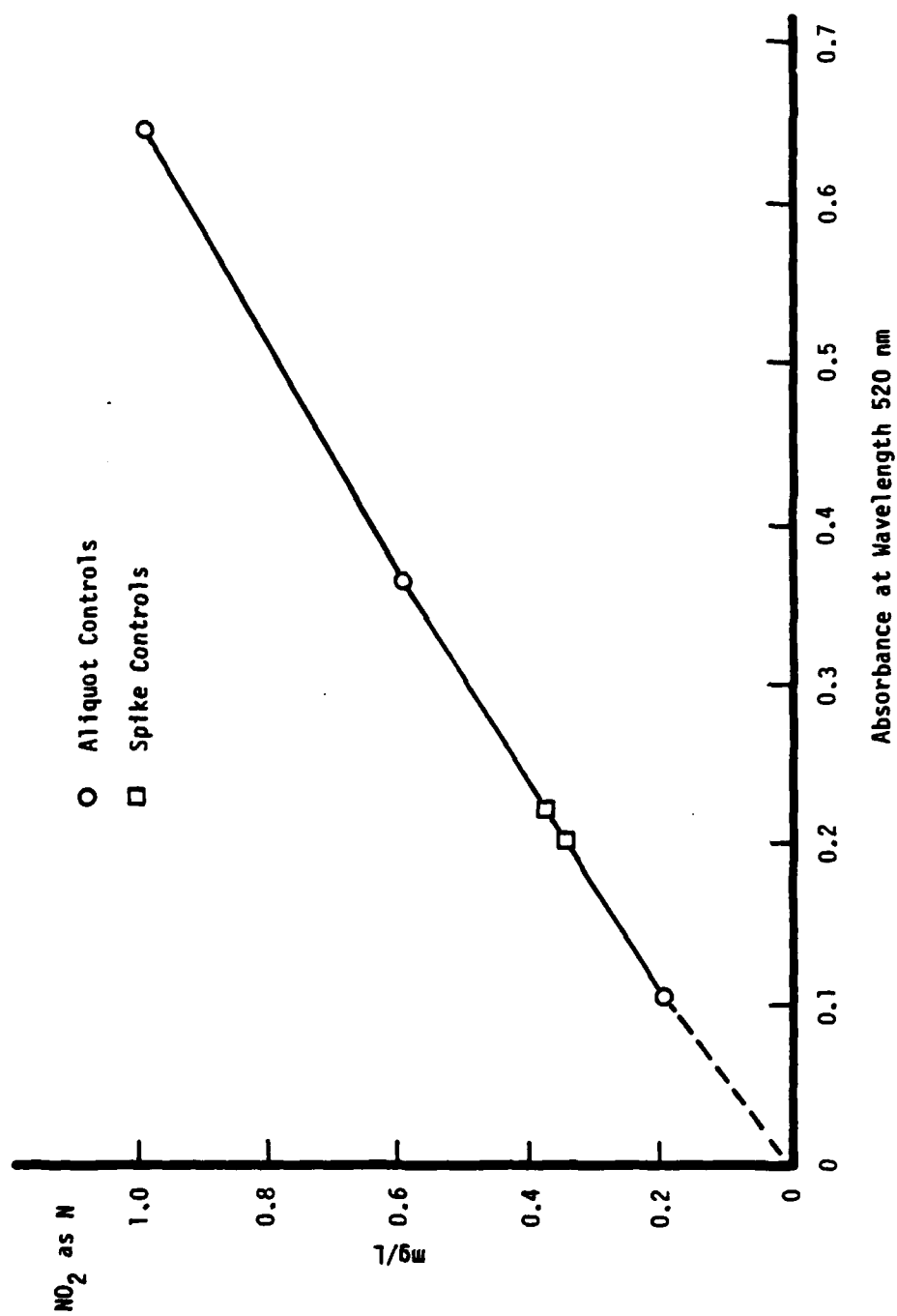
Figure 7. Calibration Curve: NO_2 or N Concentration Versus Absorbence

Table 14

COMPOSITION OF FIXATIVE - NC SLUDGE MIXTURES

Mix No.	Basic Formula	Wt %* NC	Observation Upon Completing Mix	Impact Sensitivity	Sympathetic Detonation
503A	$CaCO_3/H_2O$	0	Very cloudy white liquid - much precipitation		
503B	$CaCO_3/H_2O$	10.5	Same as above		
503C	$CaCO_3/H_2O$	10.5	Same as above		
503D	$Celite/H_2O$	0	Cloudy liquid, most celite precipitated to bottom		
503E	$Celite/H_2O$	10.5	Same as above	All Negative	All Negative
503F	$Celite/H_2O$	10.5	Same as above		
429D	$Na_2SiO_3/CaCl_2$ PC/H_2O	0	Control		
513A	$Na_2SiO_3/CaCO_3$ PC/H_2O	5.4	Muddy liquid. Dries crumbly dirt-like substance		
513B	$Na_2SiO_3/CaCl_2$ H_2O	0.7	Becomes glass-like solid		
513C	$Na_2SiO_3/CaCl_2$ H_2O	0.071	Becomes glass-like solid		

PC = Portland Cement

*Dry estimate based on 55 percent water content.

The 513 series and mix number 429D were prepared using a Waring, variable-speed, two-beater mixer. The sodium silicate and water were mixed thoroughly, followed by Portland cement if the formulation called for it. The calcium compounds were mixed in last because they tended to thicken the mixture to a highly viscous or semi-solid state. Final mixing had to be accomplished by hand using a metal spatula. The mixtures were spread out 1/4-inch to 3/8-inch thick on a shallow aluminum pan and placed under a hood to cure at room temperature. After cure, the material was crumbled and underwent several washings through an 0.45-m filter before being submitted to further testing.

5.3.1.4 EP Toxicity Test Results: Summary and Conclusions

Table 15 summarizes the leaching results for this series of experiments. The conditions and assumptions for calculating the quantities of NC extracted are discussed below. Estimated rather than exact quantities are provided for the NC fines because of uncertainties in the NO_2 content of the various particle size fractions of the RAAP products.

The conditions for calculating the NC extracted during the EP Toxicity Test were:

1. Analysis of leachate from EP-Toxicity Test was conducted by Method 353.2, EPA 600/4-79-020. The method is based on the release of nitrite ion from nitrocellulose (NC) in the presence of strong base (NaOH). NC is measured colori-metrically as nitrite, by diazotizing with sulfanilamide and coupling with N-(1-Naphthyl)-Ethylenediamine Dihydrochloride to form a highly colored azo dye.

2. For Hercules Smokeless Powder, Type A, the assumption used was that this grade of NC contains 12.6 percent N as NO_2.

3. (a) For RAAP Fines, the particle size and percent N as NO_2, as functions of weight distribution, were taken as reported in MRI Report ADA036151, June 7, 1976:

Table 15

NITROCELLULOSE (NC)-CONTAINING SLUDGES "FIXED" WITH CEMENTITIOUS MATERIALS AND CONTROLS

EP-Toxicity Test Summary

Batch No.	NC Type		NC Content* (%)	Binder Contains			Controls	EP Toxicity Test Summary		EP Toxicity Test Specimen***	
	RAAP Fines	Hercules Smokeless Powder Type A		Sodium Silicate	Portland Cement	Celite	Calcium Carbonate	NC Extracted, Range** (ppm)	Final pH	Total NC Available (ppm)	Quantity NC Extracted (%)
503A			0				X	0	7.5	0	0
503B	X		10.5				X	0.1 to 0.3	7.5	5250	0.002 to 0.005
503C		X	10.5				X	0.1	7.4	5250	0.002
503D			0			X		0	4.6	0	0
503E	X		10.5			X		1.1 to 4.7	4.4	5250	0.02 to 0.09
503F		X	10.5			X		0.3	4.4	5250	0.007
4290			0	X	X			0	10.7	0	0
513A	X		5.4	X	X			24.3 to 27.0	9.2	2700	0.9 to 1.0
513B		X	0.7	X				1.0	10.5	350	0.3
513C		X	0.07	X				0.2	10.5	35	0.7

*Based on dry NC

**See assumptions used for RAAP NC Fines and Hercules Smokeless Powder in text.

***100-g specimen in 2-L final volume.

Fraction	Particle Size (μ)		Weight Distribution (%)	% N as NO_2
1	>88		66	12.87
2	<88	>44	23	13.43
3	<44	>5	11	11.59
4	<5	>0.8	0.1	11.59
5	<0.8	>0.2	<0.1	4.0
6	<0.2		0.1	3.39

(b) Any one of the following five conditions could have occurred at the conclusion of the EP Toxicity Test:

(1) NC particles from Fraction 6 only entered the leachate for nitrite analysis. Hence, the conversion factor for (N as NO_2)/NC is 0.0339.

(2) NC particles (or their degradation products) which entered the leachate were equally divided between Fractions 5 and 6. The corresponding conversion factor N/NC now becomes: $(3.39 + 4.10)/2 = 3.75\% = 0.0375$.

(3) NC particles (or their degradation products) which entered the leachate were equally divided between Fractions 4, 5 and 6. The conversion factor now becomes:
$(3.39 + 4.10 + 11.59)/3 = 6.36\% = 0.0636$.

(4) NC particles or their by-products which entered the leachate followed the total size distribution shown in the reference report. The N/NC factor is now:
$(0.66)(12.87) + (0.23)(13.43) + (0.11)(11.59)$
$+ (0.001)(11.59) + (0.001)(4.0) + (0.001)(3.39)$
$= 12.88\% = 0.1288$.

(5) All NC particles or their by-products came from Fraction No. 2, the fraction with the highest percent N as NO_2. Hence, N/NC = 0.1343.

A simple algorithm which was derived to allow for each of the assumptions described above facilitated the reduction of the data, as presented in Table 15.

It is apparent from Table 15 that the percentages of NC leached are considerably higher for the polysilicate -- and polysilicate/ Portland cement -- fixed materials than the controls. The result may be attributed to the greater alkalinity of the cementitious mixtures (pH 9.2 to 10.7) than the controls (pH 4.6 to 7.5), which would tend to denitrate the NC by removal of nitrate groups. Until the ultimate fate of the released nitrate (presumably converted to nitrite) group is understood, it is not clear whether the degradation is deleterious or beneficial, from an environmental viewpoint.

5.3.2 Fixation of NC with Epoxides

5.3.2.1 Description of Formulations Investigated

The technical approach set forth during this part of the laboratory effort consisted of treating nitrocellulose with an amine-cured epoxide. Amine-cured epoxides were selected and recommended for study as candidate fixative agents for contaminants of an organic nature. This selection stemmed from an extensive survey of state-of-the-art fixation processes during Phase I of the project. In the selection process, major emphasis was given to the following criteria: utilization of an E/F agent that presented a high probability of chemically reacting with organic contaminants; ease of processing; low cost of materials; and desirable physical and mechanical properties of the fixed-waste product.

Amine-cured epoxides, as a class, were expected to provide enhanced stabilization of organic contaminants. The epoxide reactants were expected to dissolve the organic contaminants. Hence, they would provide an appropriate matrix to effect molecular dispersion necessary to effect "chemical" fixation. Enhanced stabilization of NC was expected to result from the creation of hydrogen bonds between the epoxide and contaminant during consolidation and cure of the three-dimensional structure.

100

In the present investigation, epoxides were formulated to readily consolidate at room temperature. In addition, they were expected to resist anticipated leaching stresses. In contrast, organic acid-cured epoxides and thermosetting polyesters give rise to bonds that are potentially hydrolyzable when exposed to water and aqueous acidic solutions.

Table 16 lists three general types of NC-Epoxide Fixed Products that were investigated. The first type consisted of epoxide - NC products made with synthetic fibers obtained from Hercules, Inc. Products were prepared by blending at room temperature with epoxide and 1-3 weight percent NC. The NC was dewatered by vacuum filtration at room temperature. Curing was also conducted at room temperature. The second type of product differed from the first in the use of NC fines obtained from RAAP in lieu of Hercules NC. The NC fines were also dewatered by vacuum filtration prior to blending and curing in the manner described above. The third type of product was prepared with NC fines, epoxides and $CaSO_4$. The purpose of incorporating $CaSO_4$ was to measure the potential effect that a common sludge inorganic ingredient would have on the processing and effectiveness (from an environmental standpoint) of the NC-Epoxide fixed product.

The epoxide employed in the present work consisted of the base resin, diglycidyl ether of bisphenol A (EPON 828) and diethylene-triamine (DETA). Figure 8 gives their chemical structures. The ratio of EPON 828/DETA employed in these studies was 85-95/5-15. In order to increase the solids loadings of the epoxide mixtures, it became necessary to reduce the viscosity of the epoxide. This was accomplished by substituting the lower molecular weight, RF-475, neopentyl glycol diglycidyl ether, for a portion of the EPON 828. An effective working ratio for our studies was EPON 828/RF-475 = 3/1. Products with high loadings of NC and other sludge solids were achieved

Table 16

EPOXIDE-NC FIXED PRODUCTS STUDIED UNDER PHASE II

Composition	Percent by Weight
1. Epoxide (amine cured)	99-97
NC Hercules	1-3
2. Epoxide (amine cured)	99-97
RAAP NC fines	1-3
3. Epoxide (amine cured)	80
RAAP NC fines	1-2
$CaSO_4$	18
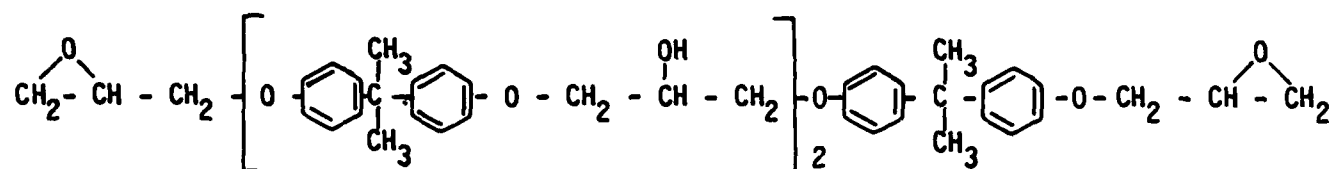
Diglycidyl ether of bisphenol A
(2,2-bis[p-(2,3-epoxypropoxy)phenyl]-propane)
(EPON 828)
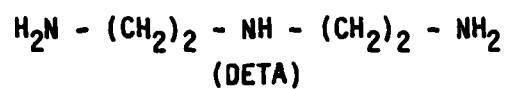
$$H_2N - (CH_2)_2 - NH - (CH_2)_2 - NH_2$$
(DETA)
Diethylenetriamine

Figure 8. Epoxy Ingredients

through the use of the lower molecular weight reactive diluent. The other compounds in the NC sludge consisted of calcium carbonate and calcium sulfate. Portland cement was included in the recipe to tie up the water present in the wet NC fines.

5.3.2.2 Laboratory Procedures

During preliminary compatibility testing of NC and epoxides, it was discovered that NC is soluble in DETA. However, solution was accompanied by an apparent chemical reaction between the two and heat build up. When dry NC was used, the reaction was violet with frothing and sizzling and, in one instance, the mix had to be aborted. Radford NC fines and Hercules smokeless powder, wet with 55 weight percent water, were dissolved in DETA at 6 percent and 18 percent, respectively, and with a controllable exotherm (uncontrolled exotherms resulted in bubble-filled cured products).

Further refinements of the recipe of the NC-Epoxide mixtures and the mixing procedure resulted in compositions containing up to 15 weight percent NC and 66 weight percent solids loadings. Table 17 summarizes the compositions of these products. The general laboratory procedure for preparing these batches is described briefly below:

> Disposable plastic beakers were used during all phases of the mixing preparations. Batch sizes of 50 grams or less were allowed to cure in the disposal beakers. Larger batches were poured onto aluminum sheets covered with another aluminum sheet, and pressed down to a thickness of 3/4 inch or less to avoid high exotherm. The epoxy and filler portions were blended separately then mixed together. The fillers were blended first and set aside. The epoxy components were then blended and immediately upon completion of the mixing, the fillers were blended in. All stirring was done by hand using glass stirring rods. The above procedure was modified slightly for formulas that called for calcium carbonate. In these formulas, the $CaCO_3$ was added to the blended epoxy components first and then the other blended fillers were added.

Table 17

COMPOSITION OF NC-EPOXY SLUDGE MIXTURES

Mix No.	Basic Formula In Grams	% NC By Weight	% Solids	Observations Upon Completion of Mix	Other Comments
0817A	Resin Epon 828 = 73.3 Hardener DETA = 7.3 NC = 9.1 H_2O = 10.3	10.2	0.0 (Binders not in-cluded)	16 hour ambient cure. Hard, semigloss, creamy tan color. No signifi-cant interior foam.	Fairly high exotherm.
0817B	Epon 828 = 61.9 DETA = 6.2 NC = 7.7 $CaCO_3$ = 15.5 H_2O = 8.7	8.47	24.2	Same as 0817A except color a lighter tan with reddish coat.	Fairly high exotherm. $CaCO_3$ added to help keep exotherm down and also as a filler.
0822D	Epon 828 = 30.0 RF-475 = 6.0 DETA = 4.0 NC = 5.0 $CaSO_4$ = 50.0 H_2O = 5.6	10.0	55.3	Two-day ambient cure. Hard, semigloss, a muddy tan. No interior foam.	Fairly high exotherm. $CaSO_4$ added in place of $CaCO_3$. Also RF-475, a diluent, introduced to the study at this time.
0824B	Epon 828 = 28.5 RF-475 = 8.2 DETA = 4.1 NC = 5.0 $CaCO_3$ = 6.2 PC = 6.1 H_2O = 5.6	10.1	28.1	Same as 0822D except for 24 hour ambient cure.	Moderate exotherm. Portland cement introduced to the study at this point.
0913A	Epon 828 = 42.0 RF-475 = 12.0 DETA = 6.0 NC = 5.0 $CaCO_3$ = 25.0 PC = 33.0 H_2O = 17.0	10.0	53.6	Rolled thin to keep exotherm down. Hard, semigloss, olive green. No interior foam, two-day ambient cure.	Exotherm hardly noticable because material was rolled thin on aluminum foil.
0914A	Epon 828 = 50.0 RF-475 = 15.0 DETA = 7.0 NC = 18.0 PC = 40.0 H_2O = 20.0	12.0	40.0	Rolled thin, semigloss. Two-day cure. Light green, no foam.	Exotherm hardly noticable.
0914B	Epon 828 = 35.0 RF-475 = 10.0 DETA = 5.0 NC = 23.0 PC = 51.0 H_2O = 26.0	15.3	51.3	Same as 0914A except color is dark green.	Exotherm hardly noticable. About 15 g of H_2O came out of the mix and was decanted off. The mix was then rolled thin.
0919A	Epon 828 = 120.0 DETA = 12.0 NC = 15.0 H_2O = 14.0	10.2	0.0	Rolled thin, hard, semigloss one-day ambi-ent cure. Creamy tan, no foam	Moderate exotherm. No filler to absorb heat.
0919B	Epon 828 = 100.0 DETA = 10.0 NC = 13.0 $CaCO_3$ = 25.0 H_2O = 14.0	8.47	24.1	Same as 0919A except color is lighter tan.	Exotherm hardly noticable.

5.3.2.3 EP Toxicity Test Results: Summary and Conclusions

Three batches of epoxy-fixed sludges containing between 8 and 10 weight percent NC (on a dry basis) and between zero and 54 weight percent solids loading were prepared for EP Toxicity Testing. The results are summarized in Table 18.

The percentages of NC leached from these epoxy-fixed NC sludges are similar to those reported for NC fixed with cementitious material containing alkaline constituents (Section 5.2.3). It was suggested before that the leaching was attributed to a degradative reaction in the alkaline media to produce soluble nitrate (and nitrite). It appears that the DETA may involve a similar de-nitration of the NC when the two compounds are admixed, even though the final pH of the mix is acidic. These observations led to the study described in the next section on the characterization, by IR spectroscopy, of the reaction product between NC and DETA.

5.3.2.4 IR Characterization of NC in Epoxy Binders: Summary and Conclusions

IR measurements were obtained on a Perkin-Elmer 327 Infrared Spectrometer. Samples were analyzed in the epoxy hardener, diethylenetriamine (DETA).[*] IR spectra were obtained for DETA (Figure 9); DETA containing 10 weight percent dry NC (Figure 10); DETA containing wet NC, or, 8.6 weight percent dry NC and 9 percent water (Figure 11); and NC fines (Figure 12). The two strong peaks at 1275 cm^{-1} and 1650 cm^{-1} and the peak at 1075 cm^{-1} were all present in Figure 12, and are in good agreement with the literature.[2] Figure 11 showed little or no evidence of these two strong peaks, but an

---

[*]Hardening or curing agent for epoxy binder.

[2]Anal. Chem., 32, (4) 495 (1960).

Table 18

EP TOXICITY TEST SUMMARY: EPOXY-FIXED NC SLUDGES

Batch No.	NC* Content Wt. %	Filler	EP Toxicity Test NC Extracted (ppm)	Final pH	Table NC Available in Test Specimen (ppm)	Quantity NC Extracted (%)
0913A	10	Calcium Carbonate and Portland Cement	63.3 - 65.9	4.9	5000	1.3
0919A	9	None	14.9 - 15.5	4.9	4500	0.3
0919B	8	Calcium Carbonate	58.1 - 60.6	4.8	4000	1.5

*Dry estimate based on 55 percent water content.
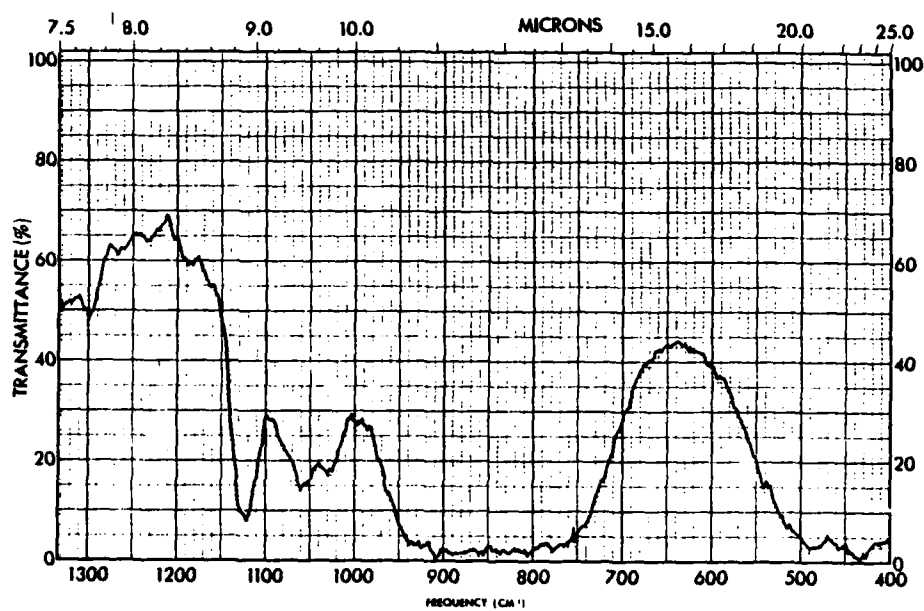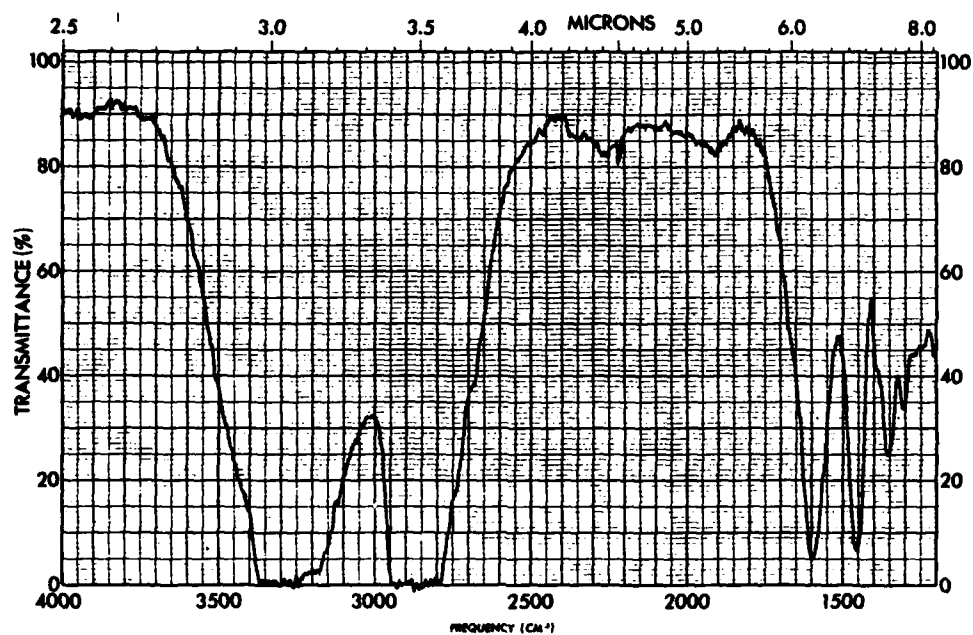
Figure 9.   IR Transmittance (%) Versus Frequency (cm⁻¹): DETA
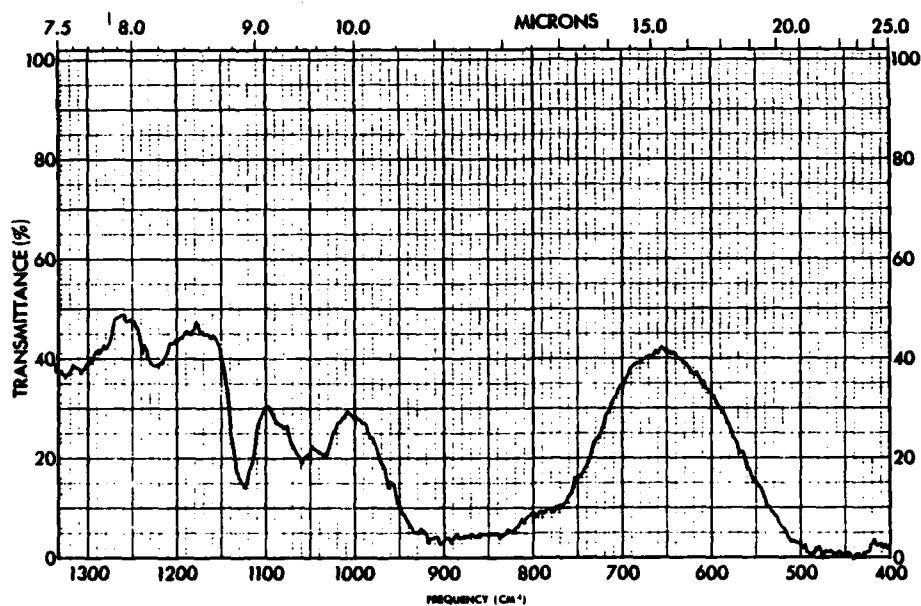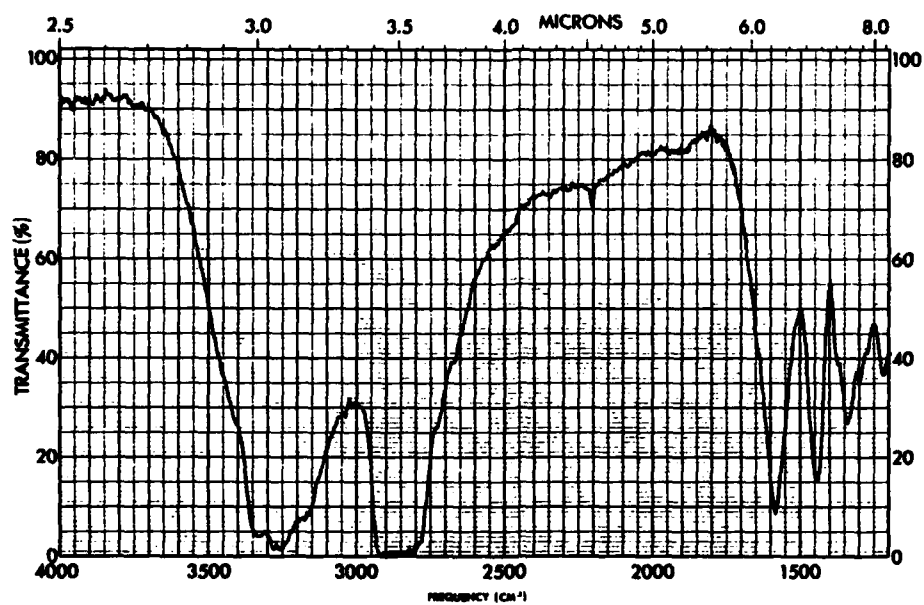
Figure 10. IR Transmittance (%) Versus Frequency (cm⁻¹):
NC (Dry) in DETA

109
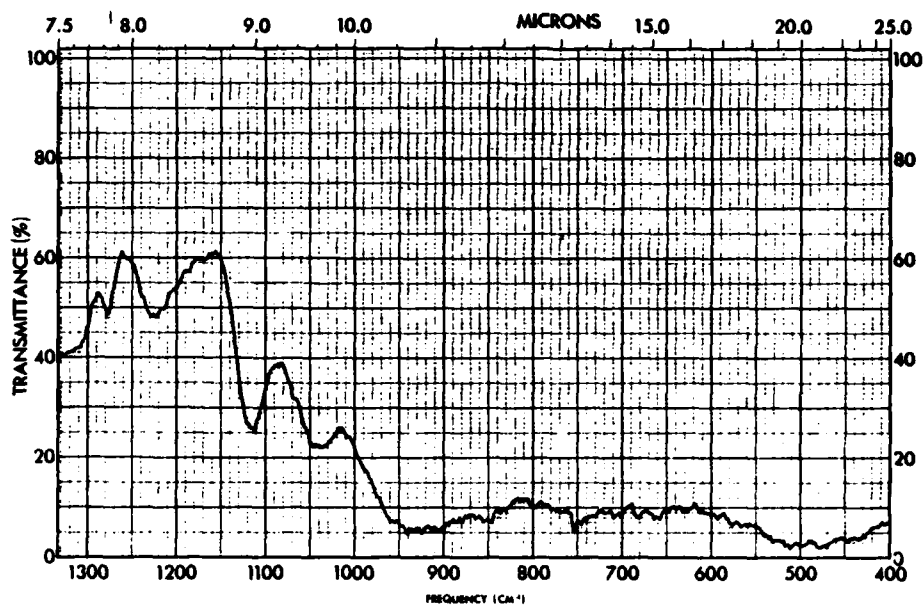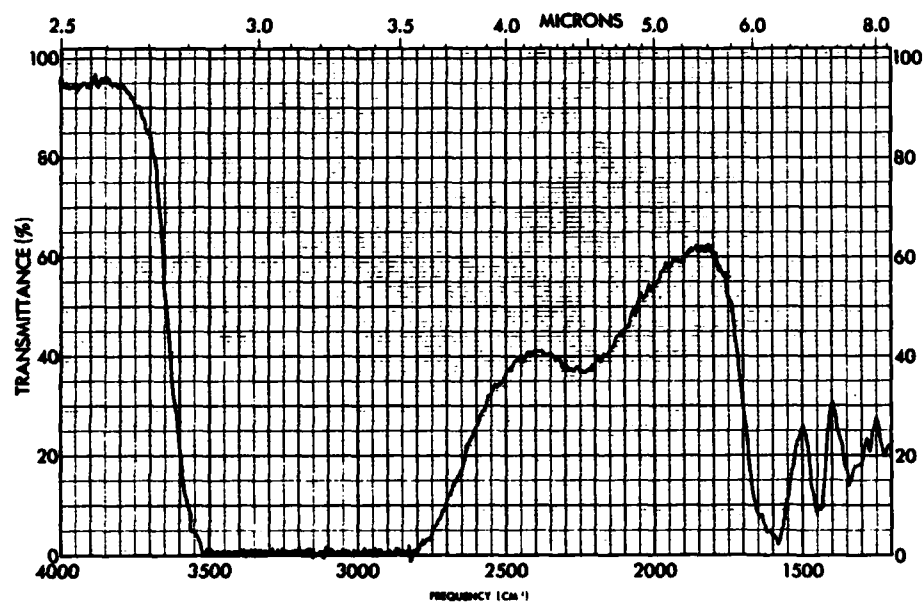
Figure 11. IR Transmittance (%) Versus Frequency (cm⁻¹):
NC (Wet) and DETA

110
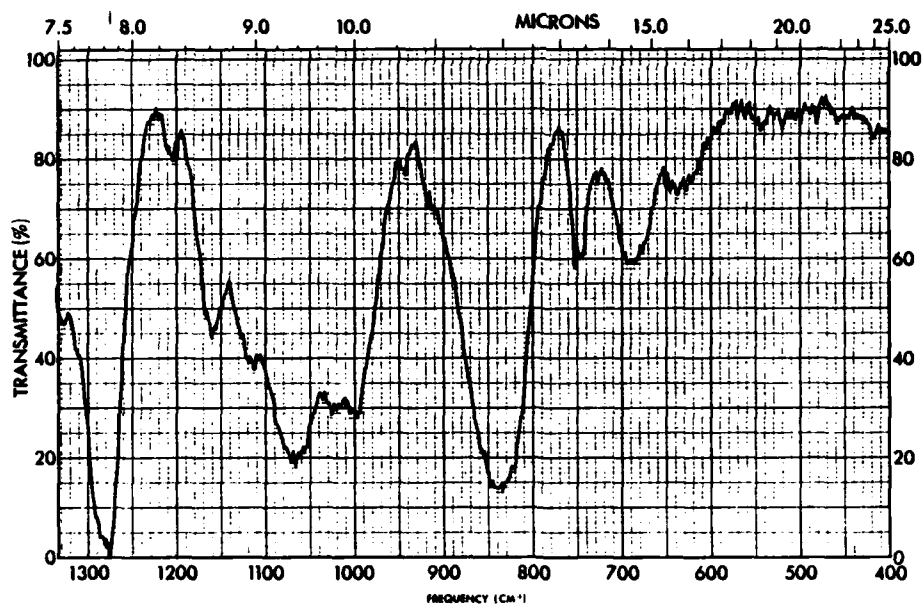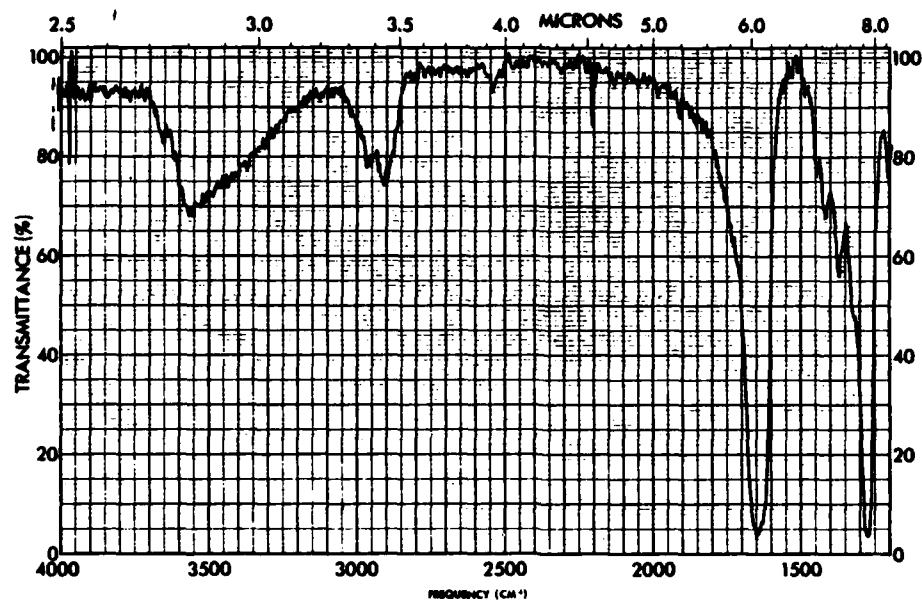
Figure 12. IR Absorbance Versus Frequency (cm^{-1}): NC (Dry)

111

unassignable small peak appeared at 1225 cm^{-1}. This suggested the disappearance of NC and the possibility of the formation of a reactant product between NC and DETA. The DETA-wet NC fines system (Figure 11) showed evidence of the presence of unreacted NC.

IR spectra were also obtained for three of the above samples in the form of KBr pellets. Figure 13 represents the spectrum of the epoxy control containing DETA. Figure 14 contains unreacted NC and DETA, the same mixtures as were seen previously in Figure 10. Finally, Figure 15 shows the spectrum of epoxy, unreacted NC and DETA in a KBr pellet. Unlike the previous results presented in Figures 9 to 12, the spectra show no significant differences. This is probably due to the low levels of NC (~1.5 weight percent) in the epoxy/KBr pellets used to determine the IR spectra.
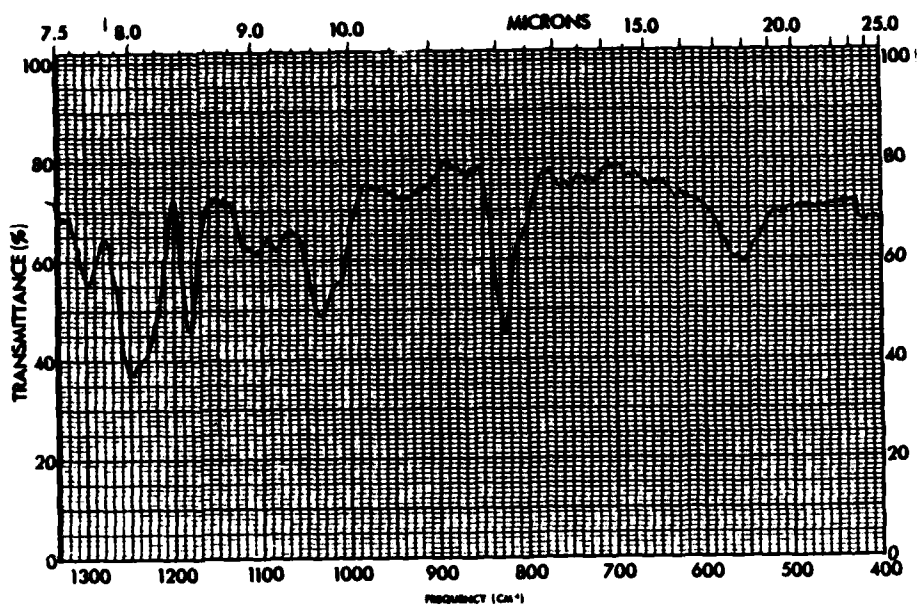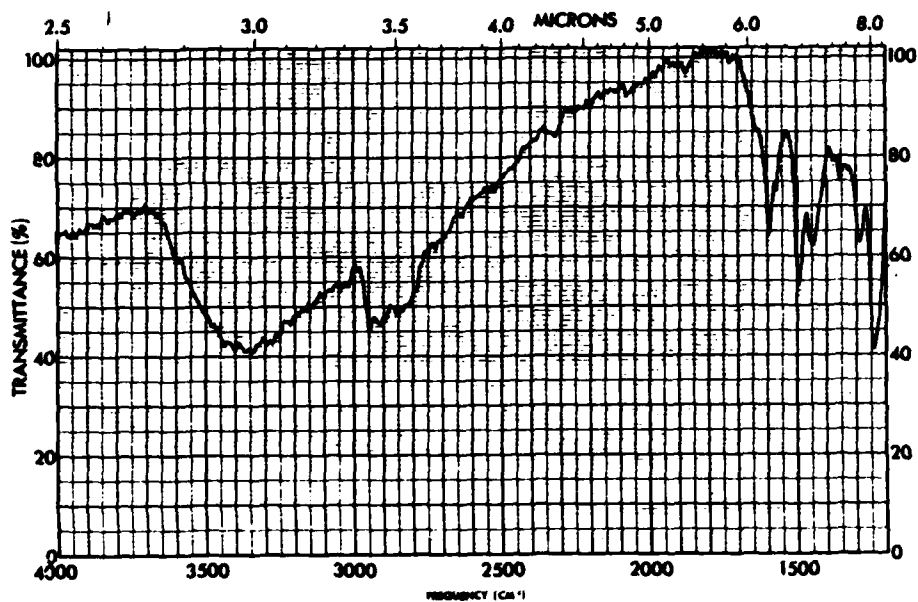
Figure 13. IR Transmittance (%) Versus Frequency (cm^{-1}):
Epoxy and DETA
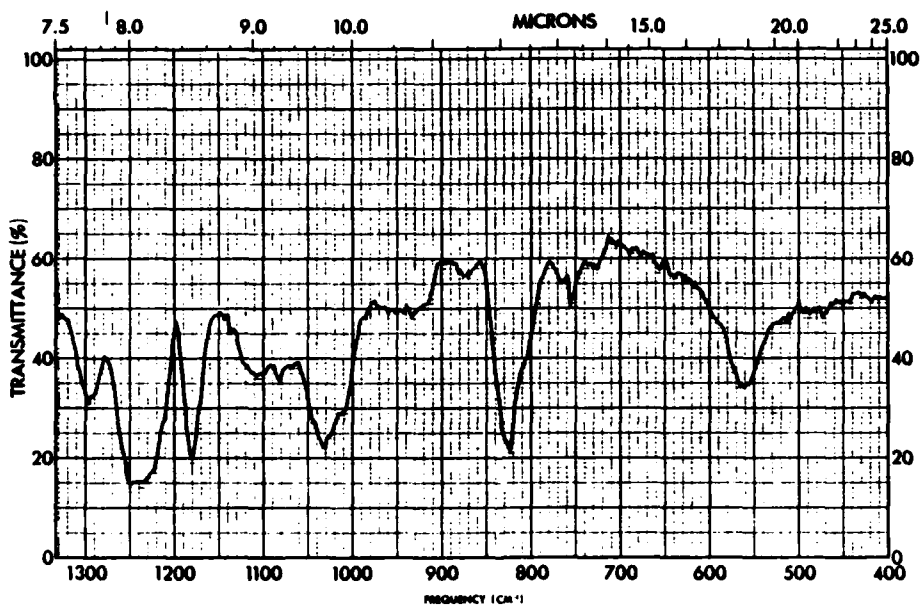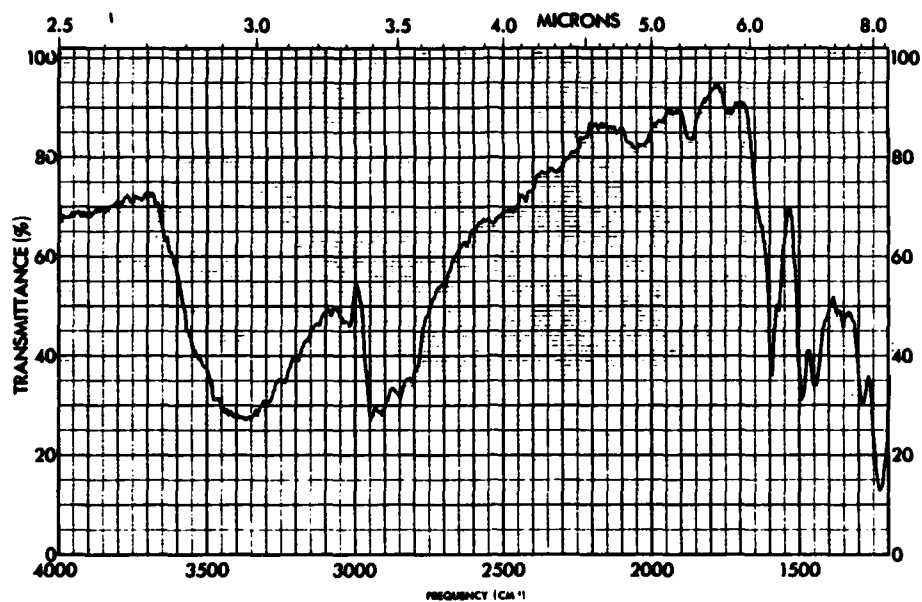
Figure 14. IR Transmittance (%) Versus Frequency (cm^{-1}):
NC (Dry) and Epoxy
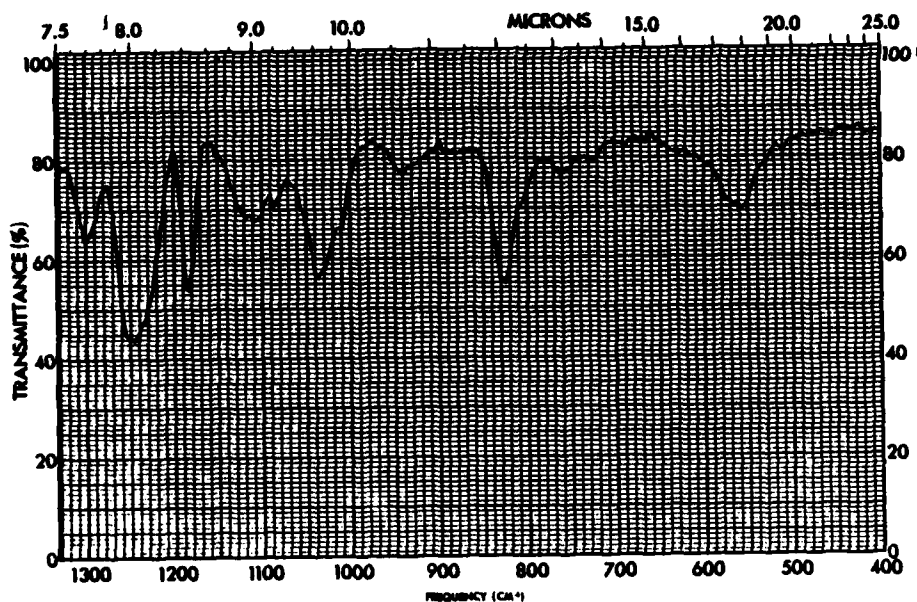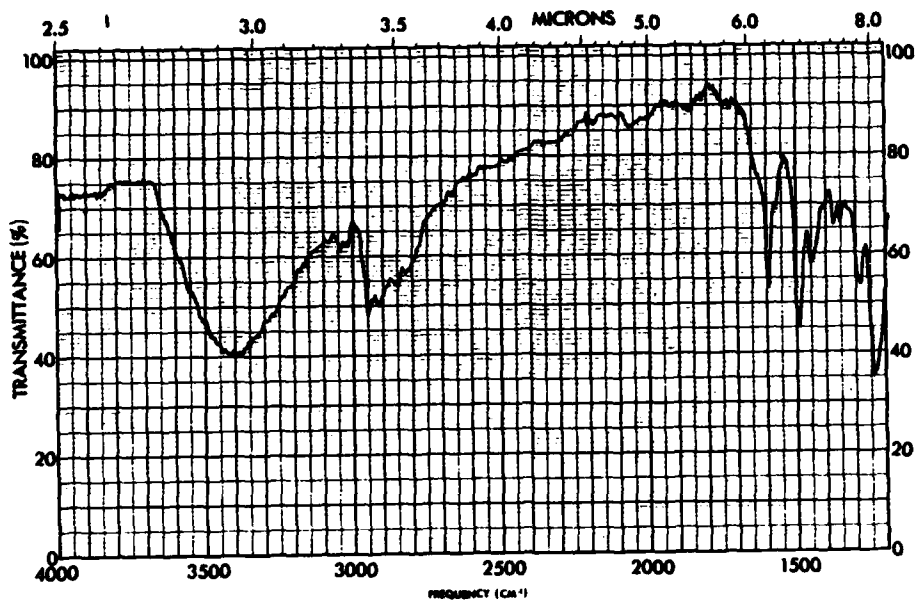
Figure 15.   IR Transmittance (%) Versus Frequency (cm⁻¹):
Epoxy and Unreacted NC

5.4 INORGANIC-TYPE SLUDGES FIXED WITH POLYSULFIDES

5.4.1 Background and Objectives

This section describes laboratory preparations and characterization studies of heavy metal contaminants stabilized by polysulfide-based E/F materials. The rationale for selection of polysulfides is presented in Section 3.0 of this report. In selecting polysulfides, emphasis was placed upon the following criteria: high probability of reacting with heavy metals to form stable insoluble products; ease of processing; low cost; and desirable physical and mechanical properties of the fixed products.

Two types of polysulfide-based E/F materials were investigated: (1) polysulfides in combination with epoxides and (2) polysulfide in combination with sulfurous materials. Polysulfides were employed to isolate toxic heavy metals from contaminated synthetic aqueous effluents. The ready rendering of pure effluents from contaminated wastewater was due to the practically complete precipitation of heavy metals in the presence of sodium polysulfide. Precipitates were readily filterable and gave rise to residues that exhibited resistance to dissolution under simulated leaching stresses. Thus, use of polysulfides accomplished two objectives: (a) formation of insoluble heavy metal polysulfide residues and (b) purified effluents.

Heavy metal polysulfides were found to consolidate readily to form monoliths in both epoxide and sulfurous matrix materials. Heavy metal polysulfides fixed in epoxide were formulated to consolidate readily at room temperature. Also, they were expected to exhibit good performance due to the good mechanical properties attributed to the resin and the chemical stability of both the heavy metal polysulfide and epoxide. Sulfurous matrix materials, although consolidated by

thermoforming, were expected to yield highly leach-resistant embodiments to the toxic heavy metals which were chemically fixed by reaction with polysulfide. Such fixed products showed plastic (ductile) behavior and were expected to preclude loss of contaminants under anticipated leaching stresses.

In the present investigation, both epoxide and sulfurous matrix materials were prepared. However, epoxides were examined in greater detail due to the processing feature of ready consolidation at ambient temperatures. Employing an epoxide binder, monoliths were prepared that contained 10 percent metal polysulfide and up to 75 percent solids loading by weight. These monoliths exhibited excellent resistance to degradation and contaminant loss under EP Toxicity Testing protocol.

Polysulfides were selected for investigation because they also offered the possibility for simultaneous wastewater treatment and sludge fixation. Consequently, fixation would be considered as part of a total system concept rather than as an after treatment. Particular emphasis was placed on electroplating sludges such as those reported for Tobyhanna Army Depot.[92] Figure 16 illustrates a conceptual-ized wastewater treatment/fixation process for electroplating wastes containing heavy metal contaminants. The flow diagram illustrates the major steps in the process. For example, electroplating wastewaters are treated with alkali metal polysulfide to precipitate toxic heavy metals. Next, standard separation techniques such as filtration or decantation are employed to separate the clarified supernatant liquid from the solidus residue; the high affinity of the S_x^{2-} anion would assure polishing of the liquid effluent to meet wastewater discharge standards such as those described in NPDES permit requirements.

---

[92]U.S. Army Environmental Hygiene Agency, "Chemical Fixation of Electroplating Wastes," Tobyhanna Army Depot, Tobyhanna, PA, July 25-29, 1977, Solid Waste Consultation No. 26-0027-78, Department of Army, Aberdeen Proving Ground, MD, pp. 1-9.
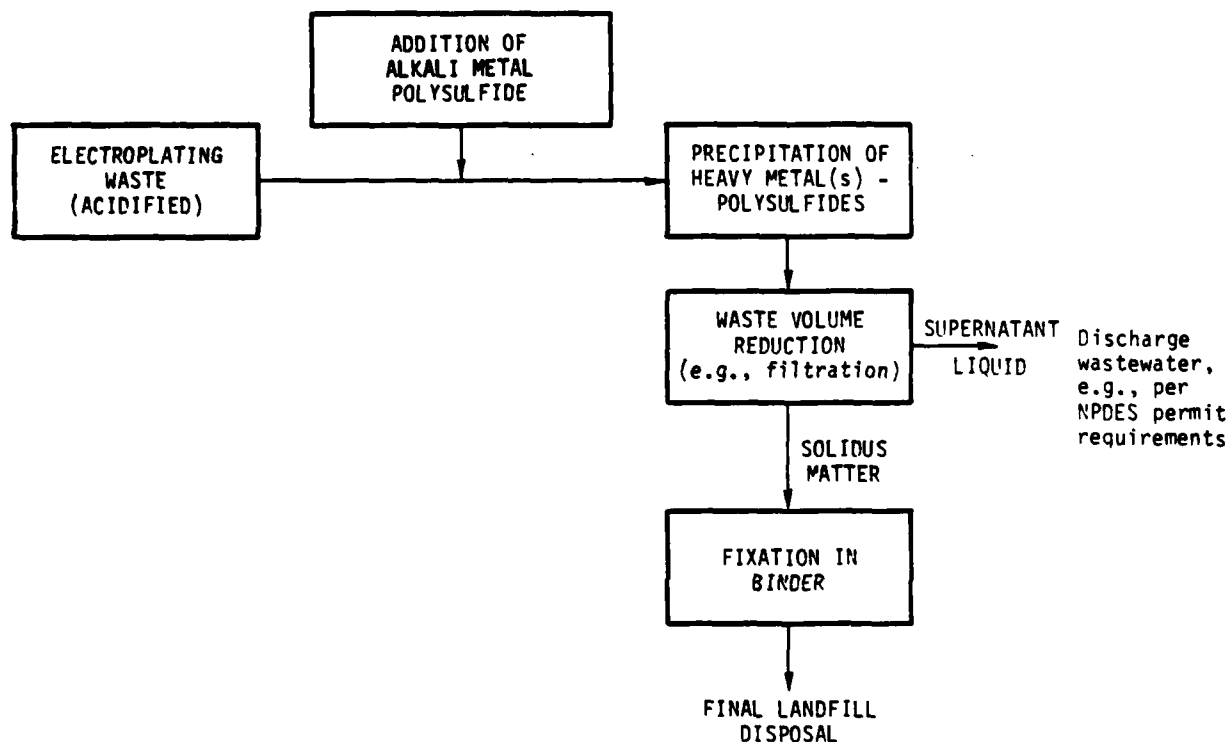
Figure 16. Conceptualized Process Flow Diagram of Electroplating
Wastes in a Polysulfide Waste Treatment/Fixation Process

Separation would result in significant waste volume reduction. Volume reduction, as described later in the cost discussion of this section, would be expected to provide considerable savings in materials, transportation and disposal costs. The concentrated, solid waste residue would be incorporated into an organic binder to produce a fixed waste product suitable for disposal in a sanitary landfill.

5.4.2 Description of Polysulfides Investigated

Most of the recent interest in the polysulfides, and in particular the alkali and alkaline earth polysulfides, stems from the thermal stability of the melts over the temperature range 230° to 484°C. This characteristic makes these materials useful as molten electrolytes for advanced batteries such as Na/S, Li alloy/FeS and Li alloy/ FeS_2.[31] For this application, however, the polysulfides are prepared in the absence of air and moisture, either by reacting the anhydrous Na_2S and liquid sulfur at elevated temperatures or by the stoichiometric reaction between Na_2S or Na and S in ethanol or liquid ammonia, followed by evaporization and crystallization. The X-ray powder diffraction patterns of some of the crystalline compounds have been reported by Rosen (1971)[71] and Nickless (1968).[61] These compounds are reputed to have the composition X_2S_n, where:

---

[31]Janz, G.J., Technical Progress Report, Thermophysical Properties of Inorganic Polysulfides, Department of Energy, Contract DE-AC02-79R10387, December 1979.

[71]Rosen, E. and R. Tegman, A Preparative and X-Ray Powder Diffraction Study of the Polysulfides Na_2S_4 and Na_2S_5, Acta Chemical Scandinavica, 25, 3329, 1971.

[61]Nickless, G., Inorganic Sulfur Chemistry, pg. 690, Elsevier Publishing Co., New York, 1968.

$n = 2$ to 5 for $X = Na, Rb$

$n = 2$ to 6 for $X = K, Cs$

$n =$ up to 9 for $X = NH_4^+$

A literature search on heavy metal polysulfides uncovered references to the crystal structures of at least six (6) different compositions of chromium polysulfide, CrS, Cr_2S_3 (two forms), Cr_3S_4, Cr_5S_6, and Cr_7S_8. The compounds were formed from the elements at high temperatures and pressures.[30] Properties of these compounds were not given.

The aqueous alkali and alkaline earth polysulfides, however, are not as well characterized as the crystalline salts prepared under non-aqueous solution.[61] Also, they are not as pure as the anhydrous salts. The impure solutions can be obtained from several commercial sources. FMC Industrial Chemical Division offers an 88 percent concentrate which is primarily Na_2S_4. Los Angeles Chemical Company produces a 29 percent solution of "mixed polysulfides." The FMC and LA Chemical Co. products are sold as agricultural fungicides and insecticides. Hence, purity is not too important. Morton Thiokol manufactures pure grades of Rank 2.25 (mainly Na_2S_2) and Rank 4 (Na_2S_4) material as intermediates for their own use in the production of Thiokol rubbers. Polysulfides also find use as modifiers in the production of craft paper.[25] Calcium polysulfide solution is recommended by the U.S. Air Force for control, decontamination and disposal of mercury.[100]

---

[36]Inorganic Chemistry, Vol. 8, No. 3, P. 566, March 1969.

[61]Nickless, G., Inorganic Sulfur Chemistry, Pg. 690, Elsevier Publishing Co., New York, 1968

[25]Gustafsson, L. and A. Teder, Thermal Decomposition of Aqueous Polysulfide Solutions, Swensk Pappaerstidning Org, 72, p. 249, May 1969.

[100]Webb, W.M., Control, Decontamination and Disposal of Mercury, Report OEHL-79-149, Brooks Air Force Base, November 1979.

Other properties of polysulfides relevant to the present study include the following: The polysulfides are reported to be hygroscopic and readily oxidized in air; the hydrolysis rates decrease in the order

$$Na_2S > Na_2S_2 > Na_2S_4 > Na_2S_5$$
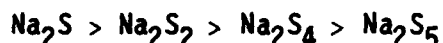
and they form insoluble precipitates with mercury, lead, cadmium, chromium and copper in aqueous solution.

5.4.3 Laboratory Procedures - Ingredients and Preliminary Tests

(a) Sodium polysulfide was prepared in accordance with reaction (a), Figure 17.[4] The procedure was as follows:

Eighty grams of sodium hydroxide beads were dissolved in water and mixed with 80 grams of sublimed sulfur. The aqueous dispersion was mixed with a magnetic stirrer and slowly heated to 100° C to 110° C for about one hour to form a homogeneous dark red-brown liquid, pH 13 and nominally referred to as Na_2S_2. This is based on the reaction,

$$6S + 6NaOH \longrightarrow 2 Na_2S_2 + Na_2 S_2O_3$$
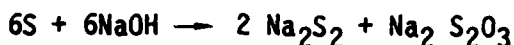
based on the stoichiometry of Arntson, 1960. The solids content of the solution was determined to be 22 weight percent. Of the commercial polysulfides described in the previous Section 5.4.1, the FMC material was utilized to the largest extent. The Morton Thiokol material was received later in the project and was evaluated in conjunction with ash from open burnings (see Section 6.0, this report). The FMC product was

---

[4]Arntson, R.H., F.W. Dickson, G. Tunell, "Systems S-Na2O-H2O and S-H2O: Application to the Mode of Origin of Natural Alkaline Polysulfide and Thiosulfate Solutions," American Journal of Science, Vol. 258, October 1960, pp. 574-582.

AQUEOUS (IMPURE)

a. $(2n + 4)S + 6 NaOH \xrightarrow[\substack{\text{heat} \\ \text{and/or pressure}}]{H_2O} 2Na_2S_{(N+1)}$ [mixtures of Na_2S_2 and Na_2S_4] + $Na_2S_2O_3$

b. $Na_2S + nS \xrightarrow{H_2O} Na_2S_{n+1}$ [mainly Na_2S_{n+1}] [mainly Na_2S_4]

ANHYDROUS (PURE)

c. $Na_2S + nS \xrightarrow[\text{or alcohol}]{\text{melt}} Na_2S_{n+1}$

Na_2S_2, Na_2S_4, Na_2S_5
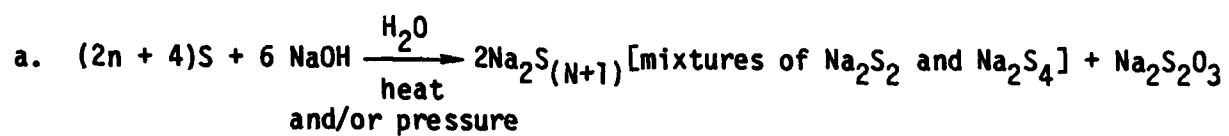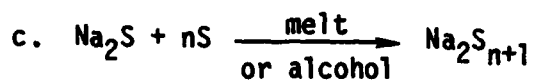
Figure 17. Preparation of Aqueous and Anhydrous Sodium Polysulfide

obtained as pellets prepared from the reaction $Na_2S + S$. It consists of 84 percent by weight "polysulfide" that is reported by FMC to be nominally Na_2S_4 and 8 percent by weight thiosulfate (although actual analysis reported by FMC shows the presence of "Na_2S_2, Na_2S_4, Na_2S_5"). Our calculations were based on this reported nominal formula and purity. The pH of this material was 11.5.

Other commercial chemicals included the following:

    Sulfur - Sublimed grade, J.T. Baker Co.
    Sodium hydroxide - reagent grade, J.T. Baker Co.

    Portland Cement
        Type I, Foreman Arkansas Cement Corp., Little Rock Arkansas

    Calcium Chloride
        MCB Manufacturing Chemicals, Inc.

    Epoxy Binder
        Resin-EPON 828 - E.V. Roberts, Santa Monica, CA
        Curative - DETA - E.V. Roberts, Santa Monica, CA
        Reactive Diluent - RF-475 - E.V. Roberts, Santa Monica, CA

    Sulfur Binder
        Sulfur - J.T. Baker Chemical Co., Phillipsburg, NJ
        Dicyclopentadiene - Conoco Chemical Co., Saddle Brook, NJ
        Vinyl toluene - Dow Chemical Co., Midland, MI
        Dipentene - Hercules, Inc., Wilmington, DE

    Heavy Metal Salts
        Nitrates of (1) lead and cadmium and (2) chromium were obtained from MCB Manufacturing Chemicals, Inc., and Mallinckrodt, Inc., respectively.

(b) Mixtures of heavy metal nitrates and calcium nitrate with FMC sodium polysulfide produced rapidly settling heavy floc precipitates with the following characteristic colors:

$$
\left.\begin{array}{ll}
\text{I} & Cr(NO_3)_3 \\
\text{II} & Pb(NO_3)_2 \\
\text{III} & Cd(NO_3)_2 \\
\text{IV} & Ca(NO_3)_2
\end{array}\right\} + \text{excess} \atop Na_2S_n \quad
\begin{array}{l}
\text{Heavy} \\
\text{Floc} \\
\text{Settles} \\
\text{Rapidly}
\end{array}
\left\{\begin{array}{ll}
\text{I} & \text{Blue} \\
\text{II} & \text{Black} \\
\text{III} & \text{Bright Yellow} \\
\text{IV} & \text{Light Yellow}
\end{array}\right\} + {\text{Orange} \atop \text{Liquor}}
$$

Precipitate

Preliminary miniaturized leaching tests with either 0.5 N acetic acid or 0.5 N nitric acid of the chromium polysulfide precipitate (I) were encouraging, as described below:

After the metal polysulfide precipitates had been thoroughly washed and dried, they underwent a distilled-deionized water wash at a ratio of 1 g of precipitate to 10 mL of water. The mixture was then controlled at pH 5, using 0.5 N acetic acid and put on a shaker. The mixture was monitored about every 30 minutes and pH-controlled at 5, if necessary. This procedure continued throughout the day and was resumed on the following work day until a 24-hour period had elapsed. At this point, enough distilled water was added to the mixture to bring the ratio of liquid to precipitate to 20 mL/1 g. The liquid was then filtered off through an 0.45 m filter for AA analysis.

The initial results after 24 hours of leaching at the three pHs shown were as follows:

	pH		Cr^{+3} PPM* in Leachate	
	Initial	24 Hours	Initial	24 Hours
Orange Liquor From I	12	12	--	0.5
Water-Washed Precipitate in 0.5 N Acetic Acid	5	4.5	0.07	0.03
Water-Washed Precipitate in 0.5 N Nitric Acid	2	2	--	5

*By flameless Atomic Adsorption Spectroscopy.

Tests for free Cr^{+3} in the liquor containing the blue precipitate showed values of approximately 0.5 ppm, tenfold less than the allowable EPA limit in wastewater. Treatment of the water-washed precipitates with acetic acid at pH 5 produced even lower levels of dissolved chromium after 24 hours of exposure. Adjustment of the pH to 2, with nitric acid, however, resulted in high levels of the dissolved metal. The results with chromium are interesting in view of the reported instability of the monosulfide in aqueous medium and the solubility of the hydroxide (amphoteric) at high pH.

It was later found that the FMC polysulfide contains approximately 8 to 9 ppm of an insoluble chromium contaminant. This does not invalidate these results for it would raise the initial metal content still further.

Preliminary evaluation was also carried out with a plasticized thermoplastic sulfur mixture for subsequent testing as a matrix for the insoluble heavy metal polysulfides. The mixture was prepared in the following manner:

The plasticized thermoplastic sulfur mixture consisted of sublimed sulfur solids (55 % by weight), dicyclopentadiene (15 %), vinyl toluene (15 %) and dipentene (15 %). The liquids were all mixed together into a uniform solution. This solution was heated to above 160° C and the sulfur was slowly mixed in. After all the sulfur had appeared to go into the solution, the mixture was poured into a shallow aluminum pan and placed under a hood to cool to room temperature to a gummy solid.

5.4.4 Laboratory Formulation

Two types of alkali metal polysulfide reagents were investigated in the laboratory, as discussed previously. The purpose of employing both reagents was to develop, simultaneously, (1) a database on use and effectiveness of commercially available material, and (2) an alternative capability to produce, as needed, sufficient quantities of alkali metal polysulfide. Greater use was made of the commercial-grade polysulfide, although limited quantitative comparison was made of the polysulfides of Pb^{+2} and Cr^{+3} using both reagents. For example, each reagent was found to produce precipitates of large particles that were readily filtered in the laboratory.

Lead, chromium, cadmium, and mixtures of the three contaminants, when precipitated with alkali metal polysulfides, were found to be compatible with both an organic epoxide binder and a sulfurous matrix. The mechanical properties of the fixed waste were shown to be as predicted for both matrices, showing that the heavy metal polysulfides neither adversely affected the curing reactions of the thermosetting resin, nor the mechanical properties of both matrix materials. Although isolation of the heavy metals and purification from the supernatant mother liquor were achieved, the experimental efforts were geared primarily to characterization of fixed waste products. Thus, examination and optimization of the stoichiometry and reaction between alkali polysulfide and heavy metals remain open areas for future work.

126

Table 19 describes the composition of the two types of binders investigated.

Various combinations of synthetic AAP sludges containing heavy metal contaminants and fillers in combination with the two types of binders were tested as shown in Table 20. Up to 10 weight percent chromium polysulfide and 75 weight percent solids were achieved with the epoxide binder.

Each binder was found to be compatible with the polysulfides of lead, chromium, cadmium, their mixtures, gypsum, and Portland cement, Type I. Gypsum was introduced as an inert filler material, re-resentative of those present in military sludges, as discussed previously. Although the matrix material (epoxide) may tolerate up to about one percent moisture, Portland cement was introduced to soak up or "chemically fix" larger quantities of free water. Fixing water in this manner eliminated the need to further dry the heavy metal precipitates. The higher processing temperatures employed with the sulfurous binders were sufficient to remove free water without requiring the use of Portland cement.

The epoxide binders, in combination with the heavy metal polysulfides, Portland cement, and other fillers, exhibited good mechanical properties, and additionally offered the process feature of consolidation at room temperature. Therefore, polysulfide-epoxide E/F products were selected for detailed EP Toxicity Testing during Phase III. Table 21 gives the formulation data for typical mixtures of fixed waste products.

Table 19

PRINCIPAL TYPES OF BINDERS INVESTIGATED

Ingredients Epoxide Binder*	Weight Percent
EPON 828	75
DETA	15
Reactive Diluent**	10

*Ambient temperature cure

**Neopentyl Glycol Diglycidyl Ether

Ingredients Sulfurous Binder*	Weight Percent
Sulfur	55 - 100
Unsaturated monomers**	45 - 0

*Thermoformed at 160-170°C.

**Dicyclopentadiene, dipentene,
vinyl toluene, 15, 15, 15, respectively[5]

Table 20

HEAVY METAL POLYSULFIDES FIXED WITH TWO BINDERS

Epoxy-Binder

Ingredient	Parts			
	I	II	III	IV
Chromium Polysulfide*	10		6	
$Cr^{+3}/Pb^{+2}/Cd^{+2}$ Polysulfide*				7
Calcium Sulfate	50	44	34	21
Epoxy	40	36	28	26
Portland Cement		13	21	31
Water		7	11	15

*Prepared from FMC sodium polysulfide

Sulfurous Binder

Ingredient	Parts	
	I	II
$Cr^{+3}/Pb^{+2}/Cd^{+2}$ Polysulfide*	10	6
Sulfur Matrix	90	51
$CaSO_4$		43
Water	**	**

*Prepared from FMC sodium polysulfide.

**Water lost at processing temperature

129

Table 21

POLYSULFIDE-EPOXIDE FIXED WASTE PRODUCT FORMULATIONS

| Experiment Number | Total Mix Wt. (g) | Components (Weight Percent) | | | | |
		Resin	Heavy Metal Polysulfide	Gypsum	Portland Cement	Water
0823A	50	40	10 (Cr)	50.0	---	---
0825B	65	30.8	6.9 (Cr)	38.5	23.8	---
0826A	50	30.6	0.5 (Cr) 6.6 (Pb) 1.0 (Cd)	24.5	24.5	12.3
0909A	125	25.0	10.0 (Cr)	21.0	34.0	10.0
0909B	175	25.0	11.6 (Pb)	21.7	35.4	6.3
0909C	125	25.0	10.0 (Cd)	21.0	44.0	---
1013B	175	25.0	10.0 (Cr)	22.9	42.1	---

The polysulfide-epoxide fixed sludges were prepared in three separate stages before being combined into a single product. The heavy metal polysulfide was prepared first. It was thoroughly washed and dried before being used. The second stage of preparation began with blending the fillers and the metal polysulfides together. The final preparatory stage consisted of mixing the epoxy compounds together. The epoxy resin was prepared last since the mixture from the second stage had to be mixed into the epoxy resin while it was still in a liquid state. Upon completion of the entire mixture, a gummy substance of the consistency of baker's dough was placed between aluminum foil and rolled out to about 1/2-inch thick to cure.

Numerous smaller size (10 g to < 100 g) batches were prepared in order to improve the processing and optimize the formulations to the high solids loadings desired.

Table 22 summarizes the range of polysulfide-epoxide fixed waste products examined. Notice that the level of solids loadings (i.e., contaminants and fillers) is in the range of 60-75 percent by weight. For waste streams containing no inert fillers, heavy metal polysulfide could, in principle, be loaded to encompass that fraction occupied by inert fillers. In addition, notice that polysulfide/epoxide-fixed waste products required only 25 percent by weight resin in order to successfully produce monolithic products.

5.4.5 EP Toxicity Test Results

A primary objective of this contract was "to ascertain the effectiveness of the fixed-waste products from an environmental standpoint." In this study, EPA's EP Toxicity Test was utilized as the primary criterion for quantification of environmental acceptability. Specifically, EP Toxicity Tests were employed for assessing the effectiveness of polysulfide-epoxide E/F materials in fixing lead, cadmium and chromium in synthetic sludges containing the heavy metal contaminants. Table 23 summarizes the EP Toxicity Test results. The data show that polysulfide-epoxide fixative materials can effectively stabilize lead cadmium and chromium when incorporated at 13,000, 72,600, and 36,400 ppms in the products, respectively.

The results of the EP Toxicity Test are quite encouraging in view of the low level of free metals found in the leachate, the relatively high weight of toxicant per weight of fixative used, and the low volume of the fixed sludge produced. As will be shown later in the discussion on cost considerations (Section 5.4.7), the total costs estimated for fixing (F) and transporting and disposing (T/D) of AAP heavy metal sludges utilizing polysulfides are approximately 1/16 (F) and 1/10 (T/D), respectively, the comparative costs for cementitious-fixed materials.

Table 22

RANGE OF POLYSULFIDE-EPOXIDE FIXED WASTE PRODUCTS EXAMINED

Ingredients, Weight Percent							Calculated Loadings, Weight Percent	
Heavy Metal Polysulfide			Epoxide	$CaSO_4 \cdot 2H_2O$	PC	H_2O	Heavy Metal in Product	Percent Contaminant Fillers in Product
CrS_x	PbS_x	CdS_x						
6.9-10.0	0	0	25-40	21.0-50.0	0-34.0	0-10	0.9-1.3	60-75
0	11.6	0	25	21.7	35.4	6.3	7.3	75
0	0	10.0	25	21.0	44.0	0	3.6	75
0.5	6.6	1.0	30.6	24.5	24.5	12.2	0.165, 4.14, 0.376, Cr, Pb, Cd, respectively	69

Table 23

EP TOXICITY TEST RESULTS FOR SELECTED
POLYSULFIDE-EPOXIDE E/F PRODUCTS

Mix No.	Toxi-cant	Metal Content in Fixed Product		Total Metal Available in EP Tox-icity Test[a]	EP Toxicity Test Summary[b]	Metal Extracted From EP Toxicity Test Specimen
		Wt %[c]	ppm	ppm	ppm	%
1013B	Cr^{+3}	1.3	13,000	650	1.1	0.17
0909B	Pb^{+2}	7.26	72,600	3630	0.5	0.01
0909C	Cd^{+2}	3.64	36,400	1820	0.7	0.04

[a] 100-gm test specimen in 2-liter final volume.

[b] Maximum allowable concentrations in EP Toxicity Test are 5, 5, 1 ppms for Cr, Pb, and Cd, respectively.

[c] Calculated:

$$\frac{formula\ weight\ metal}{formula\ weight\ metal\ nitrate} \times \frac{weight\ metal\ nitrate}{total\ weight\ of\ metal\ polysulfide}$$

$$\times \frac{weight\ of\ metal\ polysulfide}{total\ weight\ of\ batch}$$

5.4.6 X-Ray Diffraction Measurements of Polysulfide Precipitates

Literature reports on the crystallinity and structure of the alkali and alkali earth polysulfides (prepared under pure and anhydrous conditions) suggested that it would be useful to determine whether the heavy metal polysulfides evaluated here were also salt-like.

X-ray diffraction measurements were made on four (4) preparations: the polysulfides prepared from Cr^{+3}, Cd^{+2}, Pb^{+2}, and a lead monosulfide control. The specimens for these preparations were coded 0926-7 (CrS_x), 0926-8 (PbS_x), 0926-9 (CdS_x), and 9026-10 PbS control. The X-ray diffraction data appear in Table 24. The results are reported by the X-ray crystallographer, were as follows:

(a) Sample 0926-7 has two unexplained peaks at 4.87 A and 4.59 A, but orthorhombic sulfur is the major crystalline phase. Lack of X-ray fluorescence blackening of X-ray film and actual chromium X-ray measurement suggest that any chromium is present as a minor constituent of this sample.

(b) Samples 0926-8 and 0926-10 have PbS as the major crystalline phase. Sample 0926-8 also has some orthorhombic sulfur and has twice as large PbS crystallite size as Sample 0926-10.

(c) Sample 0926-9 has a very diffuse ß CdS, which is a major phase. $Cd(OH)_2$ appears to be a minor phase, although its sharp peaks allow it to be seen. The two shades of color in this sample suggests that proportions of these two phases observed will vary with sampling.

(d) Very microcrystalline or amorphous phases can easily hide in the background and therefore cannot be excluded. X-ray diffraction should reveal new peaks when a major crystalline phase is prepared. [Suggests Sample 0926-7 may contain microcrystalline or amorphous chromium compound(s)?]

The results are equivocal and firm conclusions cannot be drawn at this time regarding the structures of these polysulfides. Very microcrystalline or amorphous phases can easily be hidden in the background, even if they were the major constituent in the samples.

Table 24

X-RAY DIFFRACTION DATA FOR HEAVY METAL POLYSULFIDES

0926-7 (CrS_x)		File 24-733 Orthorhombric Sulfur	
I	d(A)	I	d(A)
2	7.70	8	7.708
8	5.78	17	5.757
6	4.87		
10	4.59		
5	4.07	12	4.060
4	3.930	16	3.918
30	3.858	100	3.854
2	3.576		
7	3.453	37	3.447
1	3.392		
7	3.342	22	3.336
12	3.218	41	3.219
5	3.116	20	3.113
3	3.082	15	3.084
8	2.851	17	2.848
5	2.627	11	2.625

0926-8 (PbS_x)		File 5-592 PbS (Control)	
I	d(A)	I	d(A)
100	3.433	84	3.429
80	2.974	100	2.969
60	2.101	57	2.099
50	1.791	35	1.790
25	1.714	16	1.714
12	1.485	10	1.484
15	1.363	10	1.363
35	1.328	17	1.327
20	1.213	10	1.212

Table 24 (Continued)

0926-9 (CdS$_x$)		File 13-226 Cd(OH)$_2$		File 10-454 CdS	
I	d(A)	I	d(A)	I	d(A)
1	11.4				
2	7.95				
2	6.15				
15	4.71	70	4.7		
3	3.619				
10 (Broad)	3.363			100	3.36
15	3.035	65	3.03		
7	2.915			40	2.90
20	2.550	100	2.55		
(Broad)	2.072			80	2.058
5	1.862	35	1.857		
(Broad)	1.762			60	1.753
6	1.751	20	1.748		
1	1.703				
2	1.641				
2	1.443	8	1.441		

Nevertheless, the presence of the unexplained peaks in the Cr^{+3} precipitate and the larger crystallite size of the Pb^{+2} polysulfide (compared to the control) are interesting findings.

5.4.7 Comparative Costs for LSAAP-Type Sludge Fixed with Polysulfide/ Epoxy, Polysulfide/Sulfur and Cementitious Binders.

Tables 25 and 26 show the comparative costs for three fixative materials: cement/sodium silicate, polysulfide/sulfur, and polysulfide/ epoxide. Notice from Table 25 that, on a per-pound basis of sludge, sulfur and epoxide appear to be progressively more expensive than cement/sodium silicate. However, Table 8 shows that if costs are compared on a per-pound-of-toxicant (Pb)-fixed basis, the order of relative costs is exactly reversed; cement/sodium silicate is 100 and 16.6 times more expensive, respectively, than sulfur and epoxide.

It may be argued, in the case of the sulfur binder, that processing costs associated with thermoforming, as well as a need for plasticizers, will raise the cost of this system compared to the other two.

Appendix B contains the engineering assumptions used to derive these cost estimates.

Other elements of costs need to be considered in comparing these systems; namely, transportation (T) and disposal (D) costs. For example, costs to transport and dispose a 50-gallon drum of LSAAP-treated sludge in the Texarkana area is stated to be $60 (Day and Zimmerman, 1982). Costs to transport and dispose of sludge in the greater Los Angeles area varies from under $7 to $110 per 50-gallon drum, depending on whether a sanitary or secure landfill is required, as shown in Table 27. Consideration of the fixed sludge density, the weight of the fixed sludge per 50-gallon drum, and the corresponding

Table 25

COMPARATIVE RAW MATERIALS COSTS OF FIXATIVES TO HANDLE ONE-POUND OF SLUDGE

Cementitious/Sodium Silicate Fixative*

$$\frac{\$89.00}{1b\ Pb \times \dfrac{300\#\ Sludge^*\ (wet)}{0.189\#\ Pb}} = \frac{\$0.056}{1b\ sludge\ (wet)}$$

Epoxy/Polysulfide

$$\frac{\$5.36}{1b\ Pb \times \dfrac{75\ Parts\ Dry\ Sludge}{(10\ Parts\ Pb\text{-}P.S.)\ \dfrac{0.62\ Parts\ Pb}{1\ Part\ Pb\text{-}P.S.}}} = \frac{\$0.44}{1b\ Sludge\ (dry)}$$

Sulfur/Polysulfide

$$\frac{\$0.89}{1b\ Pb \times \dfrac{60\ Parts\ Dry\ Sludge}{(10\ Parts\ Pb\text{-}P.S.)\ \dfrac{0.62\ Parts\ Pb}{1\ Part\ Pb\text{-}P.S.}}} = \frac{\$0.92}{1b\ Sludge\ (dry)}$$

---

*Mixture ratio 300 sludge (wet):170 Portland Cement and sodium silicate, Day and Zimmerman, Inc. (LSAAP), "Chemical Fixation of Sludge," no date, Page 27.

Table 26

COMPARATIVE RAW MATERIALS COSTS OF FIXATIVES TO HANDLE <u>ONE POUND OF LEAD</u>

Fixative Type		Unit Cost	Fixative/Pb Ratio	$ Fixative/lb Pb
Cementitious/Sodium Silicate		$0.10/lb	890	$ 89.00
Treatment Chemicals		< $0.01/lb		---
Total Cost				$ 89.00
Epoxy/Polysulfide:	Epoxy	$1.20/lb	4.0/1	$ 4.80
	Sodium Polysulfide	$0.67/lb	0.84/1*	.56
Total Cost				$ 5.36
Sulfur/Polysulfide:	Epoxy	$0.05/lb	6.5/1	$ .33
	Sodium Polysulfide	$0.67/lb	0.84/1*	.56
Total Cost				$ .89

<hr>

*To fix 1 lb Pb requires 0.84 lb Na_2S_4

Table 27

COSTS TO TRANSPORT AND DISPOSE OF WASTES IN GREATER LOS ANGELES AREA

	Sanitary Landfill (50-Gallon Drum)	Secure Landfill (50-Gallon Drum)
Transportation (T)	$5.41	$10
Disposal (D)	$1.28	$20 to $100
Total T and D	$6.99	$30 to $110*

*Note: $60 for LSAAP Sludge in Texarkana area per Day and Zimmerman Report, 1982.

Table 28

COMPARATIVE COSTS TO TRANSPORT (T)/DISPOSE (D) LSAAP-TYPE FIXED WASTE (SANITARY LANDFILL)

	Present Cementitious Process	Polysulfide/Epoxy Process
Density of Fixed Sludge, lb/gal	19	12.8
Weight of Fixed Sludge, lbs per 50-gallon drum	950	640
Weight of Lead in Fixed Sludge, lbs per 50-gallon drum	0.38	39.7
Estimated T&D Costs per lb lead*	$17	$0.17

*Based on $6.69 T&D costs per drum.

weight of lead in the 5-gallon drum, the estimated T&D costs for the cementitious-fixed LSAAP sludge may be seen to be ten times greater than for the corresponding epoxy-polysulfide fixed material (see Table 28).

5.4.8 Summary and Conclusions

Commercially available sodium polysulfide and a laboratory preparation of this material have been used successfully to chemically fix synthetic AAP sludges containing heavy metals. The chemically fixed sludges were embodied in both epoxy and sulfurous matrices and cured at ambient temperature and by thermoforming methods, respectively. The epoxy/polysulfide-fixed material was tested by the conventional EP Toxicity Test and the leachates after testing were below the maximum EPA allowable concentrations for Cr, Pb and Cd. While the results of X-ray diffraction measurements on the heavy metal polysulfides were equivocal, it is possible that structures characteristic of these materials may be present.

Comparative costs for LSAAP-type sludges fixed with epoxy/polysulfide appear to be considerably lower than for the conventional cementitious-fixed material. Additional studies of these promising materials are warranted and are recommended.

141

6.0 PHASE IV - ADDITIONAL STUDIES

Phase IV, Additional Studies, was added later in the project. It provided for additional effort to investigate several related topics not included in the original scope of work; namely,

(1) Examine for the effects of common ions, mixed metals, ionic strength, pH, and buffering action, the insoluble compounds which are formed when AAP sludges containing heavy metal contaminants are "fixed" with silicates and/or cements.

(2) Perform laboratory tests on synthetic military ash waste residues (which result from open burning operations) to chemically fix the material with polymeric matrices, such as polysulfides and polyepoxides, and determine the leachability of the best formulations.

(3) Screen commercial polymers for ability to react chemically with and bind specific toxicants found in military wastes. Perform literature search to select commercially available monomers and pre-polymers with the desired functional pendant groups capable of reacting with AAP toxicants. Test candidate materials in the laboratory in combination with representative inorganic and organic contaminants.

6.1 BACKGROUND

Work under the present contract centered on <u>chemical</u> fixation rather than on physical processes, such as micro-encapsulation or surface encapsulation - in accordance with the Statement of Work. Greater emphasis was placed on:

(1) Fixing AAP sludges containing heavy metal salts (and nitrocellulose) with cementitious and siliceous fixatives over organic polymeric materials for the following reasons:

    a. Promising results were reported at LSAAP and at other Army production facilities on the use of these materials to fix AAP sludges containing heavy metal salts.

    b. Processing techniques are relatively simple and processing equipment is widely available.

    c. The cementitious-siliceous materials are generally inexpensive, readily available, and nonflammable.

Our studies under the present contract have suggested (as shown in Section 5.0) that synthetic AAP sludges containing heavy metal contaminants are not truly chemically fixed by the cementitious-siliceous materials. Instead, the metals appear to be present as highly insoluble compounds (hydroxides, silicates, carbonates) in strongly alkaline buffered medium provided by the cementitious ingredients themselves. Consequently, AAP sludges treated in this manner meet the EP Toxicity Test requirements by containing more than sufficient alkali to (a) neutralize the acetic acid used by the EP Toxicity Test, and (b) maintain an alkaline pH during the leaching. Equivalent performance in the EP Toxicity Test of cured and uncured cementitious/siliceous-treated sludges support this hypothesis. Physical measurements using Infrared, Scanning Electron Microscope and X-ray techniques did not reveal the presence of new compounds or crystalline structures indicative of chemical fixation (Section 5.2.4.1).

Also selected as part of the Test Plan for this project were investigations of:

    (2)   Amine-Cured Polyepoxides for fixing nitrocellulose via hydrogen bonding of the molecularly dispersed organic contaminant nitrate groups to pendant hydroxyl groups in the polymeric matrix, and

    (3)   Inorganic Polysulfides for chemically fixing heavy metal salts and then (a) mixing the polysulfides with epoxy materials and curing at ambient temperatures, or (b) thermoforming mixtures of the polysulfides with sulfur and curing into ductile monolithic structural forms.

The apparently successful reports from the field on the treatment of AAP sludges containing heavy metals with alkaline-buffered cementitious fixatives prompted the question of the useful life of the treated materials in soil. This led to the first task in Phase IV, as discussed in the next section of this report.

The promising results with polysulfides and polyepoxides and aqueous sludges containing heavy metal contaminants encouraged exploring the applicability of these fixatives to ash residues from open burnings of military wastes - the second task in Phase IV. And, finally, the commercial availability of polymeric materials, containing known chemically reactive functional groups capable of forming chemical bonds with contaminants found in military wastes, constituted the third task in this phase of the contract.

6.2 EFFECT OF CHEMICAL FORMS OF CONSTITUENTS AND OTHER FACTORS CONTROLLING THE SOLUBILITY OF HEAVY METAL CONTAMINANTS IN SOIL

6.2.1 Background and Objectives

The results of studies under this contract with cementitious-siliceous systems suggested that it is possible to convert heavy metal sludges into concentrated suspensions of stable insoluble compounds, e.g., hydroxides, carbonates, silicates, etc. Furthermore, by incorporating highly alkaline solids, such as Portland cement, into the mix it is possible for the resultant sand-like products to be highly resistant to leaching with acetic acid. For example, synthetic AAP sludges containing as much as 35,000 mg/L lead, as the mixed lead precipitates, and adjusted to pH 11 with Portland Cement have shown favorable results in the EP Toxicity Test (Reference Section 5.2.3, this report).

It was also determined, experimentally, that one gram of Portland Cement is capable of neutralizing over 20 mL of 1.0 N-hydrochloric acid. This is a ten-fold increase over the maximum equivalent quantity of acetic acid per gram of specimen employed in the EP Toxicity Test. Hence, the addition of Portland Cement or other substances of high alkalinity should be of value in providing a "sink" for acid, thereby preventing solubilization of the alkaline precipitates.

This approach to stabilization is not unlike, in principle, the use of antioxidants in rubbers and plastics which degrade or deteriorate in air or oxygen, particularly at elevated temperatures. The quantities of antioxidant used are less in the aforementioned application than are the quantities of buffered alkali discussed here. Nevertheless, once the antioxidants are consumed (by oxidation), the materials will degrade upon further exposure to oxidizing conditions.

Determination of the nature of the heavy metal precipitates in cementitious-siliceous systems should provide useful information on the efficacy of this approach for possible long-term exposure under varying soil conditions. In order to carry out this study, GEOCHEM,[84] a multipurpose computer program for calculating the equilibrium speciation of the chemical elements in a soil solution, was investigated for applicability to describing (and predicting) the insoluble heavy metal compounds found in AAP sludges.

6.2.2 GEOCHEM

The method of calculation employed in GEOCHEM is based on chemical thermodynamics. For each component of a soil or aqueous solution, a mole balance equation is set up, and thermodynamic equilibrium constants, corrected for ionic strength, are incorporated into the various terms of this equation according to the law of mass action. The solution of the set of nonlinear algebraic equations that results from mole balance simultaneously applied to all the components ultimately provides the concentration of each dissolved, solid, and adsorbed species in the soil system under consideration. Some typical relevant applications of GEOCHEM would include: (1) prediction of the concentrations of inorganic and organic complexes of metal cations in a soil or aqueous solution, (2) prediction of the fate of a pollutant

---

[84]Sposito, G and S.V. Mattigod, GEOCHEM: A Computer Program for the Calculation of Chemical Equilibrium in Soil Solutions and Other Natural Water Systems, University of California, Riverside, California, 1980 (Appendix D).

metal added to a soil or aqueous solution of known characteristics, and (3) estimation of the effect of changing pH, ionic strength, redox potential, water content, or the concentration of some element on the solubility of a chosen chemical element in a soil or aqueous solution.

GEOCHEM is a modified version of the computer program REDEQL2, which was developed at the California Institute of Technology by F.M.M. Morel, R.E. McDuff, and J.J. Morgan.. The detailed structure of REDEQL2 has been described in several published articles (Morel and Morgan, 1972; Morel, et al., 1973; Morel and Yeasted, 1977)[57,55,56] and in two reports (McDuff and Morel, 1973, Ingle, et al., 1978).[50,29] The methods of numerical analysis employed in the program are discussed by Morel and Morgan (1972) and are compared with the methods used in other computer programs by Leggett (1977).[39] GEOCHEM differs from REDEQL2 principally in the following ways:

---

[57]Morel, F., and J. Morgan, A Numerical Method for Computing Equilibria in Aqueous Chemical Systems, Environ. Sci. Technol., 6:58-67, 1972.

[55]Morel, F., R.E. McDuff, and J.J. Morgan, Interactions and Chemostasis in Aquatic Chemical Systems: Role of pH, pE, Solubility, and Complexation, In P.C. Singer (ed.), Trace Metals and Metal-organic Interactions in Natural Waters, Ann Arbor Science, Ann Arbor, Michigan, pp. 157-200, 1973.

[56]Morel, F.M., and J.G. Yeasted. On the Interfacing of Chemical, Physical, and Biological Water Quality Models. In I.H. Suffet (ed.), Fate of Pollutants in the Air and Water Environments, Part 1. Adv. Environ. Sci. and Technol. 8:253-267, 1977.

[50]McDuff, R.E., and F.M.M. Morel, Description and Use of the Chemical Equilibrium Program REDEQL2, Tech. Rpt. EQ-73-02, Calif. Inst. Tech., Pasadena, California, 1973.

[29]Ingle, S.E., M.D. Schuldt, and D.W. Schults, A User's Guide for REDEQL, EPA, U.S. Environ. Prot. Agency Rpt. EPA-600/3-78-024, Corvallis, Oregon, NTIS PB 280 149, 1978.

[39]Leggett, D.J., Machine Computation of Equilibrium Concentrations -- Some Practical Considerations, Talanta 24:535-542, 1977.

(1) it contains more than twice as many thermodynamic data, (2) it utilizes thermodynamic data that have been critically selected especially for soil systems, (3) it contains a method for describing cation exchange, and (4) it employs a different subroutine for correcting thermodynamic equilibrium constants for the effect of nonzero ionic strength.

It was felt that a multiple equilibria program such as GEOCHEM could be used to model or predict the solubility of different "encapsulated" metals. Since the number of metals and ligands, as well as their concentrations, can be varied, the system could potentially model such situations as:

(1) A simple metal with an encapsulating material such as sodium silicate,

(2) Multiple metals with multiple encapsulating materials such as several metals with silicate and carbonate,

(3) An encapsulated metal system undergoing an Extraction Procedure (EP) test, and

(4) An aqueous solution or encapsulated system in contact with a particular soil such as might occur in a holding pond.

6.2.3 Computer Studies

An effort was made to make a preliminary assessment of the program's effectiveness in the first three areas listed above. The assessment was limited to simple aqueous solutions and no oxidation-reduction, surface adsorption or mixed solids were permitted. The pH was fixed in all cases, although calculations were attempted for a series of different pH's from 12.0 to 3.0. Ionic strength was also kept constant throughout all calculations, although more than one ionic strength was used.

The predictions of the different systems that were modeled are given in Table 29. Complete predictions were made from pH 3 to 12 for four situations, and from pH 8 to 12 for one additional system.

147

Table 29

GEOCHEM PREDICTIONS OF LEAD DISTRIBUTION FOR
DIFFERENT ENCAPSULATED SYSTEMS

	Distribution (%)									
pH	3	4	5	6	7	8	9	10	11	12

1. Pb, Na, Ca, SiO₃, Cl IS=0.6*

	3	4	5	6	7	8	9	10	11	12
Lead Silicate (Solid)						98.4	99.9	100.	100.	93.5
Lead Hydroxide (Complex)				0.5	6.2	0.4				
Lead Chloride (Complex)	60.6	60.6	60.6	60.3	57.0	0.7				
Lead (Free)	39.4	39.4	39.4	39.2	36.8	0.4				

2. Pb, Na, Ca, SiO₃, Cl IS=2.0

	3	4	5	6	7	8	9	10	11	12
Lead Silicate (Solid)					22.4	98.9	99.9	100.	100.	99.4
Lead Hydroxide (Complex)				0.4	3.8	0.3				0.6
Lead Chloride (Complex)	83.4	83.4	83.4	83.1	61.8	0.7				
Lead (Free)	16.5	16.5	16.5	16.4	12.0	0.1				

3. Pb, Na, Ca, SiO₃, Cl, Ac IS=0.6

	3	4	5	6	7	8	9	10	11	12
Lead Silicate (Solid)							98.3	100.	99.9	93.0
Lead Hydroxide (Complex)						0.2				7.0
Lead Chloride (Complex)	30.9	3.3	0.7	0.5	0.5	0.5				
Lead Acetate (Complex)	48.7	94.7	98.9	99.1	99.2	99.0	1.6			
Lead (Free)	20.4	2.0	0.4	0.3	0.3	0.3				

4. Pb, Na, Ca, SiO₃, Cl, CO₃ IS=2.0

	3	4	5	6	7	8	9	10	11	12
Lead Silicate (Solid)										
Lead Carbonate (Solid)				90.3	99.9	100.	100.	99.8	99.9	99.9
Lead Hydroxide (Complex)										0.1
Lead Chloride (Complex)	83.2	83.2	83.2	8.1						
Lead (Free)				1.6						
Lead Carbonate (Complex)	16.7	16.7	16.7					0.2	0.1	

5. Pb, Cd, Cr, Na, Ca SiO₃, Cl, CO₃ IS=6.92

	3	4	5	6	7	8	9	10	11	12
Lead Carbonate						100.	100.	100.	100.	
Cadmium Carbonate (Solid)						100.	100.	100.	100.	
Chromium Carbonate (Solid)					100.	95.6	100.	2.0		
Chromium Hydroxide (Solid)								98.0	99.7	

*IS = Ionic Strength

Although additional combinations of ions were studied, the program failed to converge and no definitive distribution of components was made. In some cases, such as with Cr and Cd in the presence of silicate in a strongly basic solution, the program arrived at an equilibrium where a hydroxide alternatively precipitated and dissolved. In a carbonate system, both ions form solid carbonates at high pH.

Although GEOCHEM calculates concentrations for the various soluble species, these results are not reported since it is felt they have relatively little significance to this limited study. Input concentrations were comparable to those used in typical laboratory experiments undertaken in Phase I of the study. These were $Pb(NO_3)_2$ 0.025 molar, $CaCl_2$ 0.12 molar, Na_2SiO_3 4.3 molar, and CO_3^{2-} 0.5 molar.

Among the simple lead systems, represented by Mixtures 1 and 2, the most notable points are: (1) at high pH, most of the lead is predicted to be present as solid lead silicate; (2) at pH 7 and below, the lead silicate breaks down and only soluble forms of lead result; (3) higher ionic strength solutions break down slower and result in lower concentrations of free lead ion and higher concentrations of soluble lead chloride complex.

To partially simulate the effect of conducting an EP toxicity test, Mixture 1 was reevaluated with acetate ion added to the mixture. The results were similar to those obtained for Mixture 1 at high pH, but the lead silicate began to break down sooner -- between pH 8 and 9 versus pH 7 and 8. Most of the soluble lead was also predicted to be in the form of lead acetate rather than lead chloride at lower pH. This suggests that the EP test would be a good predictor of solubility, provided the buffering capacity of the system could be overcome so that close to a neutral pH could be achieved. In other words, the system is very effective in solubilizing metals, so metals that pass the test

should be effectively "locked up." In previous laboratory studies it proved impossible to lower the pH of the system significantly within the volume constraints of acetic acid that could be added. This limitation in the test results is an artificial success that does not realistically follow natural conditions as has been discussed previously.

Because Portland cement is a complex mixture of carbonates, oxides and other materials, and can vary considerably from mixture to mixture, it was impossible to model an exact metal-Portland cement-silicate system such as proposed for use in Army Ammunition Plants (AAPs). As an alternative, carbonate ion was included in the calculations. The predictions based on these calculations are given in Table 29 under Number 4. At high pH the lead carbonate equilibrium dominates and almost all the lead is present in a solid form as Pb CO_3. Between pH 6 and pH 7 the carbonate begins to break down and the concentrations of complexed lead chloride and free lead ion closely resemble the concentrations in the lead-silicate system with comparable ionic strength.

The GEOCHEM program appears to have potential for predicting metal behavior in holding ponds or where various metals are mixed with potential encapsulating materials such as sodium silicate or Portland cement. The program is limited in that not all the thermodynamic data that are needed are currently in the data file. For example, equilibrium constants for chromium silicate and cadmium silicate are not provided. However, it is possible to add new or updated thermodynamic data as they become available. In the systems containing carbonate (such as cement systems), the calculations appear to be dominated by carbonate compound formation and the lack of data is less significant. Because of the extemely large or small size of some of the equilibrium constants and the large number of variables used in the program, the results do have an associated uncertainty. It was not possible to predict this uncertainty based on the limited testing that

150

was done. The full capability of the program -- for instance, predictions based on contact with various soil types -- was also not explored.

6.2.4 Laboratory Studies

A limited number of laboratory tests were undertaken in an attempt to evaluate whether GEOCHEM's predictions could be validated. In these experiments, a mixture of lead nitrate, sodium silicate and calcium chloride were mixed together at approximately the concentration levels used in the modeling studies given in Section 6.2.3. The initial mixture had a pH of approximately 11. This solution was split into four equal parts and the pH of each mixture was adjusted using nitric acid. The pH was monitored for 24 hours and adjusted again as necessary. Since the most significant change in the concentration of soluble lead was expected to occur around pH 7-8, an effort was made to adjust the pH to near these levels. The highly basic nature of sodium silicate as well as its buffering capacity and tendency to form silicic acid gels made simple representative experiments difficult.

The different mixtures "set up" and two phases resulted; an opaque gel with free water on top. The greater the acidity of the initial mixture, the larger the amount of free water. Unlike the experiments conducted in Phase II, the excess water was not allowed to evaporate because GEOCHEM's predictions are based on an equilibrium situation. The assumption was made that the free water and gel had achieved equilibrium after two to three days, but this fact was not experimentally verified. The gel was also analyzed by taking one gram of gel and shaking it in 20 mL of water, filtering, and making atomic absorption spectroscopy measurements (see Tables 30 and 31).

6.2.4.1 Experimental Procedure

The experimental program was limited to two series of similar, but not identical experiments and the results were generally inconsistent. The experimental procedure for the first series of experiments began with the preparation of a stock batch in a 1000-mL beaker. The following chemicals were weighed out and poured into the beaker in the order of addition indicated: (a) 272 g Na_2SiO_3 (Baume 40), (b) 128 g distilled/deionized H_2O, (c) 3.2 g $Pb(NO_3)_2$, and (d) 5.32 g $CaCl_2$

The mixture was stirred using a magnetic stirrer throughout the mixing procedure until the $CaCl_2$ was added, at which point the mixture gelled to a near solid state. The mixture had to be stirred by hand at this point for about 15 minutes, or until it returned to a fairly viscous liquid state. The mixture was then split up into four equal parts and stored in 250-mL bottles. One bottle was sealed immediately. The other three underwent various pH adjustments using 50 percent nitric acid before being sealed. The bottles were then allowed to set for two days, when the mixtures were observed to separate into two phases: free water in the upper layer and white gel at the bottom. The free water was decanted and mixed with deionized water in a 1:1 ratio. One gram of gel was mixed with 20 g of deionized water and put on a mechanical shaker for one hour. All samples were then filtered through a 45-μm filter before undergoing AAS analysis.

The second series of experiments were performed in essentially the same manner as described above, with the following exceptions: (a) the amount of deionized water used in the stock batch was raised from 128 g to 230 g, (b) the mixture did not get to a consistency that warranted hand stirring after the addition of the $CaCl_2$, as had occurred in the first series, and (c) the bottles were sealed for two days before the pH was adjusted, in contrast to immediate pH adjustment in the first series.

6.2.4.2 Experimental Results

Experimental results can be seen by comparison of the data in Tables 30 and 31. Because no measurements were made of total volumes or weights, no attempt was made to achieve a mass balance. The most relevant factor in comparing Tables 30 and 31 to Table 29 is the trend in lead concentration with pH, especially for the free water concentration. The results in Table 30 show the pattern GEOCHEM predicted. Under basic conditions, the concentration of soluble lead is relatively constant, but is lowest at highest pH. This changes dramatically between pH 6-8. The lead that was tied up as lead silicate in the gel was not extractable under the relatively mild conditions used in the study.

Table 31 shows the results of the second series of experiments. The amount of water used in mixing the components was slightly greater, but the amount of sodium silicate, lead nitrate and calcium chloride used were identical to before. The pH was controlled within a narrower range. Three significant differences from the results are reported in Table 30. First, the free water lead concentrations at acidic pH do not show a dramatic rise. Although the Table 30 results were at a slightly lower pH, this is not felt to fully explain the differences. Second, the pH of the solution obtained from extraction of the gel is relatively constant and highly acidic. Unlike the first experiments, the difference between the gel-extracted water and the free water is dramatic. Third, and not surprisingly, given the low pH of the extraction water, the concentration of soluble lead is very high. This suggests little, if any, of the lead had formed insoluble lead silicate. The results suggest that the gel in the second case was primarily silicic acid, while in the first it was lead silicate. No explanation for this difference is readily apparent since the two mixtures were made under comparable conditions.

153

Table 30

pH AND SOLUBLE Pb CONCENTRATIONS FOR SIMULATED ENCAPSULATED SYSTEMS
(Series 1)

Free Water		Gel	
pH*	Pb Concentration (ppm)	pH*	Pb Concentration (ppm)
10.8	72	10.3	34
9.	0.4	10.1	52
8.3	0.5	8.7	26
5.9	620	7.5	56

Table 31

pH AND SOLUBLE Pb CONCENTRATIONS FOR SIMULATED ENCAPSULATED SYSTEMS
(Series 2)

Free Water		Gel	
pH*	Pb Concentration (ppm)	pH*	Pb Concentration (ppm)
8.8	0.6	1.4	4400
8.0	0.8	1.3	4400
7.0	2.9	1.3	4400
6.2	8.7	1.2	4600

*pH measurements were approximate and are generally felt accurate only to ± 0.3 pH units.

The significant differences in the two systems suggest that one or the other system had not achieved equilibrium or that minor differences in mixture preparation can have a major impact or results. The results of the first series of tests was very encouraging and suggested that GEOCHEM may be effective in predicting the release of lead or other metals from encapsulating materials. The second set of experiments do not support this conclusion. Considerably more work under controlled circumstances must be done to validate GEOCHEM's predictive potential for these type systems, especially systems as complex as those of silicate gel systems. A large number of assumptions were made in both the computer simulations (chiefly assumptions that limited system variability) and the laboratory experiments (chiefly, assumptions were made with respect to equilibrium and the simplicity of the system). Further work would need to include consideration of these areas.

6.2.5 Conclusions and Recommendations

The program GEOCHEM was explored as a means of predicting metal concentrations and soluble metal behavior in a simulated encapsulated environment. The results appear to be promising and may offer a means to estimate the environmental availability of different metal species. Laboratory experiments that attempted to validate the predictions of GEOCHEM gave inconsistent results, although some results appear to track program predictions fairly well as a function of pH. The complexity of silicate gel systems complicated the particular system chosen for study.

The limited scope of the present study prevented a complete assessment of GEOCHEM's capabilities. However, the program would appear to hold considerable promise and it should be more completely evaluated. Several areas that should be considered for future work include:

155

(1) Additional thermodynamic data should be researched and included in the GEOCHEM data base.

(2) The more complex metal-Portland cement-silicate system should be examined. Different Portland cement compositions reflecting the half dozen or so major cement types could be used.

(3) The effect of acidic conditions on solubility needs to be more fully explored since the greatest release of material occurs below pH 7.

(4) The possible applicability of GEOCHEM to holding pond situations could be evaluated. This might include use of the soil interaction terms in the program.

(5) A more thorough series of experiments should be designed and carried out to verify model predictions. These would simulate any type of encapsulating system.

6.3 FIXATION OF AAP ASH RESIDUES FROM OPEN BURNINGS OF MILITARY WASTE

6.3.1 Background and Objective

Work on Phases I through III under the present contract was limited to military-derived sludges. Moreover, the literature search previously conducted under Phase I of this contract indicated increasing interest in incineration and continuing activity in open burning as a means of both destroying organic toxicants and concentrating hazardous wastes in general.

Open burning of spent charcoal containing adsorbed nitrobodies associated with the production of NG, TNT, HMX/RDX and other hazardous materials is still practiced at a number of AAP plants. Ash generated from open burnings may still contain incompletely combusted reactive organic (and possibly toxic) materials and may require further treatment prior to ground disposal. Sludges containing heavy metal contaminants and/or mixtures of organic and inorganic (heavy metal) contaminants may contain, after open burning, both incompletely combusted organic material and metallic oxides.

Since these wastes already exist in non-aqueous and concentrated form, they are admirably suited to chemical fixation by polymeric matrices such as polysulfides and polyepoxides. It is noteworthy, (as discussed earlier in Section 5.4.7) that the cost-effectiveness of organic polymer fixatives improves as the waste approaches the "ultimate" form, i.e., concentrated, low-volume, non-aqueous. Actual, representative military ashes were preferred for this study over synthetic materials made in the laboratory. One such ash, NG "slumps" was made available by the Army for this study.

6.3.2 Work Procedures and Tests

Approximately eighty (80) grams of NG "slumps" ash were received from RAAP. The ash residue was derived from open burnings of a mixture of NG waste (from the casting and manufacturing areas), sawdust and waste propellant. The ash, according to Mr. L. Smith of RAAP, was free of NG and NC (by thin-layer chromatography) but may have contained small amounts of lead, copper, diphenylamine and trace quantities of other contaminants.

A cold water slurry of the ash had a measured pH of 10.5. Heavy metals analysis by Atomic Absorption Spectroscopy (AAS) of a solution of the ash, following acid digestion,[16] showed 6.1 ± 0.3 percent lead by weight.

Tests for cadmium and chromium were negative by AAS. Impact sensitivities tests of the vacuum-dried ash, using the procedure described in Section 5.3.1.1, were negative when compared to a PETN control (Table 32). Bench studies were then carried out to encapsulate/fix (E/F) the lead contaminant in the ash with polysulfide and epoxy fixatives, as discussed below. Batch size was limited to under 20 g because of the limited quantity of ash that was available. In addition, a modified, miniaturized version of the EP Toxicity Test was employed to determine the efficacy of the various E/F procedures investigated.

The modification included, in addition to reducing batch size, using the same _relative_ quantities of treated ash, 0.5 N acetic acid and deionized water, as specified in the standard EP Toxicity Test procedure. Furthermore, alkaline chemical additives were not utilized

---

[16]Digestion in Paar Bomb with Fuming Nitric Acid Followed by Hydrofluoric Acid Per _Anal. Chem._, 45, 611 (1973).

Table 32

IMPACT SENSITIVITES OF RAAP NG "SLUMPS" ASH

Specimen*	Weight (g)	Height (cm)	Result**
PETN Control	.0204	35	D
PETN Control	.0206	30	ND
RAAP "NG Slumps" Ash	.0208	100	ND
RAAP "NG Slumps" Ash	.0206	100	ND

*Vacuum dried two hours at 100°C

**D = Detonation; ND = No Detonation

in the E/F procedure in order to ensure leaching at pH = 5 ± 0.2. Hence, buffers and other materials which would raise (or lower) the pH above (or below) the target value were avoided in these tests. Also, all solid test specimens were ground to the EPA-specified size before leaching by the miniaturized procedure.

6.3.2.1 Experimental Procedure - Preliminary Testing of Morton Thiokol Sodium Polysulfide

Preliminary tests were conducted with two (2) commercial sodium polysulfides manufactured by the Morton Thiokol Company of Moss Point, MS. These products, referred to as Rank 2.25 and Rank 4 polysulfides, consisted largely of Na_2S_2 and Na_2S_4, respectively. However, these were not pure materials and each probably contained, as impurities, small quantities of the other and possibly some of the pentasulfide, Na_2S_5. Nevertheless, these were both believed to be superior to the sodium polysulfides evaluated previously because they were used by Morton Thiokol as chemical intermediates in the production of Thiokol rubbers.

(a) Analyses for heavy metal impurities by Atomic Absorption Spectroscopy (AAS) showed the presence of 8-ppm and 5-ppm lead, respectively, in the Rank 2.25 and Rank 4 materials. Chromium and cadmium were absent in both.

(b) The polysulfides were tested with chromium nitrate by mixing 13 g of polysulfide with 12 g of a chromium nitrate solution which contained 120 g of chromium nitrate per liter. The products were compared qualitatively with chromium polysulfide prepared from sodium polysulfide made in the S-CUBED laboratory. It was noted that chromium polysulfide precipitate prepared from the Rank 2 product and the S-CUBED material appeared similar, qualitatively (dark blue-yellow color, pH < 12). Chromium polysulfide prepared from Thiokol's Rank 4 product was yellow-olive in color and pH < 12.

Other similarities were noted between the Rank 2.25 and S-CUBED's sodium polysulfide when washing the corresponding chromium precipitates. The precipitates were washed six times using 50-mL deionized-distilled water each time until the last wash water was visually clear. Removal of unreacted chromium nitrate was observed by Atomic Absorption Spectroscopy. It was found that "chromium disulfide," prepared separately from sodium disulfide Thiokol Rank 2.25 and the S-CUBED material, washed free of unreacted chromium nitrate more readily than "chromium tetrasulfide," prepared from the Rank 4 material.

(c) It was reported previously (Section 5.4.3) that chromium forms the hydroxide in alkaline medium and in presence of S^- ion. The hydroxide, however, is amphoteric and redissolves as a complexed chromium cation with the addition of excess alkali.

Attempts were made to differentiate between chromium hydroxide (I) and chromium polysulfide (II) by forming I and II, separately, at a pH close to 13 and determining the concentration of free chromium in each of the products. I and II were prepared as follows:

Chromium hydroxide (I): 50-mL deionized-distilled water, 16-mL NaOH and 21-mL $Cr(NO_3)_3$ solution were mixed together on a hot plate and heated to simmer point while stirring. The mix was then allowed to cool.

Chromium polysulfide (II): 25-mL of the cooled chromium hydroxide II and 25-mL of Thiokol Rank 4 were mixed together on a hot plate to simmer while stirring. Mix was allowed to cool before handling.

Free soluble chromium in the liquor from I was found to be 240 ppm by Atomic Absorption Spectroscopy. A mixture of the basified solubilized chromium and sodium polysulfide solution (Rank 4), at the same pH as in I and heated in a similar manner, produced a precipitate

161

(II) in which the liquor contained only 3-ppm free chromium by AAS. This result indicates that the reaction product(s) between chromium and sodium polysulfide in II is (are) different than I.

6.3.2.2 Experimental Results - Morton Thiokol Sodium Polysulfides

It was concluded from these tests that the Morton Thiokol Rank 2.25 sodium polysulfide probably is similar to the material produced at S-CUBED. Also, the test results, while not conclusive, suggest that the product formed between chromium nitrate and sodium polysulfide (Rank 4) is less soluble at very high pH than chromium hydroxide and may be chromium polysulfide. The chromium polysulfides were concluded to be acceptable for the encapsulation/fixation bench tests described in the next section.

6.3.3 Laboratory Studies - Encapsulation/Fixation Bench Tests

6.3.3.1 Experimental Procedure

Small (under 20 g) batches were prepared from the ash using three encapsulation/fixation procedures:

(1) Ash fixed in epoxy binder (29:71 weight percent ratio).

(2) (a) Ash treated with dilute acetic acid to dissolve lead.
     (b) Dissolved lead from 2(a) converted to lead polysulfide.
     (c) Treated ash from 2(a) and lead polysulfide precipitate from 2(b) mixed, washed and dried.

(3) Same as (2) and fixed with epoxy binder.

(4) Ash control.

Each of these procedure is described, briefly, as follows:

(1) A small batch of epoxy mix was prepared from Epoxy 828, DETA and R-475 in the proportion, by weight, 70:20:10. Five (5) grams of this binder were weighed out while still in the liquid state. A total of 12.4 g of ash was slowly stirred into the 5 g of binder until the compound became a gummy solid which was then pressed to about 1/4-inch thickness between aluminum foil. A 4-g portion of the pressed material was removed and placed in a 100° C oven for 20 minutes to cure.

(2) Ash weighing 5 g underwent pH-controlled leaching for 24 hours. A total of 0.54 g of Thiokol Rank 2.25 was added to the leaching liquid containing the ash and the entire mixture was then placed on a shaker for 30 minutes and allowed to settle for one hour. The precipitate was filtered and washed four times and vacuum dried at 40° C.

(3) A small batch of epoxy was prepared and 0.4 g of this binder was weighed out while still in the liquid state. A 1-g portion of the vacuum-dried sample described in (2), above, was granulated by hand and mixed with the 0.4 g of epoxy. This compound was pressed to about 1/4 inch between aluminum foil and oven cured at 100° C for 25 minutes.

(4) A 1-g sample of ash was weighed out directly from the container in which it was received and underwent pH-controlled leaching for 24 hours.

Following cure, leaching tests were performed with an 0.5 N acetic acid - deionized water mixture using the same relative quantities of materials as specified in the EP Toxicity Test. These may be described as follows:

One gram of sample was added to 10 mL of distilled deionized water. The mixture was adjusted to pH 5 using 0.5 N acetic acid and put on a mechanical shaker for 24 hours. The mixture was monitored during this shaking period to maintain a pH of 5 ± 0.2 and 0.5 N acetic acid was added, as necessary. At the end of the 24-hour period, additional distilled deionized water was added to adjust the total amount of mixture to 1 g of sample and 20 mL of liquid. The mixture was then filtered through a Millipore vacuum device using an 0.45-micro filter. The filtered liquid was analyzed for lead by AAS.

163

6.3.3.2 Experimental Results

The results of the leaching tests for each of the E/F procedures described above are summarized in Table 33, where the following may be seen:

(a) Lead chemically fixed as lead polysulfide (2,3) is more effective than the lead (presumably lead oxide) in its original chemical configuration (4).

(b) Chemically fixed lead polysulfide, alone or cured with epoxy resin, is more effective than lead (oxide) cured with epoxy resin (1).

6.3.4 Conclusions and Recommendations

It appears from limited testing of small quantities of RAAP NG "slumps" that heavy metal contaminants (e.g., lead) in the residual ash from open burnings can be stabilized by chemical fixation of the metal to the insoluble polysulfide. Miniaturized leaching tests conducted at pH 5, and which simulate the EP Toxicity Test, are encouraging.

Additional studies are recommended using larger quantities of materials. Of special importance are increased knowledge of (a) the chemical identity and form of the heavy metal contaminant(s) in the ash and (b) the conditions necessary to convert the metal(s), quantitatively, to the polysulfide form. Following successful demonstration of the method, cost-benefit analyses should be performed and compared with other approaches.

Table 33

LEACHING TEST RESULTS: NG "SLUMPS" ASH FIXED IN VARIOUS BINDERS

Description	Visual Appearance and Texture	Lead in Leachate (ppm)
Ash Cured in Epoxy Binder	Brown solid with black specks, very hard	30
Ash Containing Lead Polysulfide	Black solid, pliable, easily indented	0.2
Lead Polysulfide plus Ash Cured in an Epoxy Binder	Brown solid with tiny black specks, very hard	10
Ash Control	Small black gritty particles, very hard	105

Notes:

(a) The epoxy resin used in the above formulas in listed below in parts by weight.

Epon 828 = 70
R - 475 = 20
DETA = 10
100

(b) Leaching conditions: Mechanical agitation for 24 hours at pH 5 ± 0.2 adjusted with 0.5N acetic acid in distilled water at a ratio of 1-g sample to 20-ml solution.

6.4 SCREENING OF COMMERCIAL POLYMERS FOR CHEMICAL FIXATION OF AAP WASTES

6.4.1 Background and Objectives

The literature search conducted under Phase I of the present contract indicated that fixatives for toxic and hazardous wastes are limited primarily to those materials which are readily available, inexpensive and can be processed by conventional techniques. Our studies with cementitious materials do not support the claims by other investigators regarding chemical fixation of heavy metal contaminants by these inorganic "fixatives." Varying degrees of success have been reported in the literature for processes utilizing thermoplastic (bitumen, paraffin, polytheylene), polymerizable (urea-formaldehyde, phenol-formaldehyde, reversible emulsion polyester) and microencapsulation/surface encapsulation techniques. However, very few studies, if any, have been directly concerned with true <u>chemical</u> fixation of chemical toxicants by identifiable, chemically reactive functional groups in the polymers. This led to the present investigation to screen candidate polymers for their specific ability to react chemically with and bind (fix) specific chemical toxicants found in military wastes such as AAP sludges.

A variety of commercial monomers and polymers are available which possess reactive pendant groups, including -COOH, -NH$_2$, -OH, $-\overset{-C-C-}{\underset{O}{}}$, -SO$_2$Cl, and other moieties capable of chemical binding to the toxicants present in military wastes. Furthermore, these commercial materials offer the following additional advantages: (a) selective solubility in aqueous and/or non-aqueous media; (b) processability as polymerizable monomers or prepolymers; (c) chemical reactivity with (heavy) metal cations and organic residues, and (d) capability of providing mixed pendant groups for multiple contaminant binding.

6.4.2 Survey of Commercial Polymers

A brief literature survey was conducted on commercially available candidate monomers and pre-polymers with desired functional pendant groups capable of reacting with and binding AAP toxicants. Considerations of cost were included in the study. Other criteria for selection included the following: The candidate fixatives were available for testing in our laboratory in combination with representative inorganic and organic contaminants. Evidence of chemical reactivity and stability of the bonds formed could be obtained from relatively simple tests of solubility, swelling, IR, and/or other physical measurements. Potential interference of curing and cross-linking by calcium and magnesium compounds and other constituents normally present in military wastes were also considered as well as the means to overcome these interferences.

The following list of potential candidate monomers, prepolymers and resins were surveyed:

- Copolymers of polyacrylic acid* and polymethacrylic acid*

- Polyacrylamides*

- Acrylonitrile copolymer

- Polyvinyl alcohol and copolymers*

- Polyepoxy resin

- Chlorosulfonated polyethylenes

- Phenolic ion-exchange resins with amino, sulfonic acid, hydroxyl or phosphoric acid functional groups

- Styrene/divinyl benzene cationic ion-exchange resins

- Styrene/divinyl benzene/vinylethylbenzene anionic ion-exchange resins

*Water soluble precursors can be insolubilized.

167

It was concluded from the survey that commercial ion-exchange resins offered the greatest potential for this investigation in view of (a) their availability from several commercial manufacturers, (b) the variety of chemical functional groups attainable, and (c) the relative ease of testing in the laboratory by standard conventional procedures.

6.4.3 Ion-Exchange Resins

The ion-exchange resins selected for testing the efficacy of chemical fixation of contaminants in simulated AAP sludges are shown in Table 34.

The ion-exchange resins chosen are all insoluble, but capable of swelling to a limited extent by proper adjustment by the manufacturer of the degree of cross-linking. The resins are primarily copolymers of styrene and divinyl benzene, with the specific functional groups introduced either before or after polymerization. For example, SO_3^- groups are normally introduced by post-polymerization treatment, whereas the conventional procedure for inserting -COOH groups is via copolymerization with acrylic acid and/or methacrylic acid.

Common cation exchangers contain the following acid groups in descending order of acidity:

$$SO_3^= \ (aryl) > SO_3^= \ (alkyl) > PO_3^= > COO^-$$
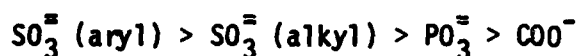
Cationic resins containing specific reactive functional groups, such as

$$C \underset{\sim NH_2}{\overset{\simeq NOH}{=}} \quad amidoxime,$$

are referred to as containing chelate functionality.

Table 34

PROPERTIES OF ION EXCHANGE RESINS

ID	Supplier	Resin Matrix	Functional Group	Particle Size (Diameter mm)	Moisture Retention %	Specific Gravity g/cm³	Operating pH	Total Exchange Capacity
Duolite CS-346	1	Crosslinked Copolymer	Amidoxime	0.2-0.6	57-59	1.15	1-11	1.3-1.5 millimoles CuO/g (pH = 4)
Duolite 466	1	Polystyrene Divinyl Benzene	Aminodiacetic (Sodium Form)	0.3-1.2	55-60	1.05	0.5-7	45 g Cu/l (pH = 4)
Duolite 467	1	Polystyrene Divinyl Benzene	Anion-Phosphonic	0.3-1.2	60-65	0.75	2-7	45 g Cu/l
Duolite 863	1	Vinyl Aromatic	None (Non-Ionic)	0.18-1.0	--	1.05	--	Variable
Duolite C-26	1	Polystyrene Divinyl Benzene	Sulfonic Acid	0.3-0.8	48-52	1.27	--	Variable
Duolite S-761	1	Crosslinked Phenol-Formaldehyde	Phenolic and Methylol	0.3-1.2	--	1.11	2-5	Variable
Duolite A-340	1	Epoxy-Polyamine	Tertiary Amine	0.3-1.2	52-58	1.13	0-9	2.4 meq/ml as CaCO$_3$
Duolite A-7	1	Crosslinked Phenol-Formaldehyde	Secondary Amine	0.3-1.2	53-60	1.12	0-6	2.4 meq/ml HCl
Duolite C-464	1	Crosslinked Polyacrylic Acid	Acrylic Acid	0.3-0.84	52-60	1.15	5-14	2.7 meq/g CaCO$_3$
Duolite ES-570	1	Crosslinked Phenol-Formaldehyde	Secondary Amine	0.3-1.2	52-57	1.12	0-6	1.6-2.2 eq/: HCl
Duolite ES-145	1	Experimental Resin	Isothiourea	--	--	--	--	--
Duolite GT-73	1	Crosslinked Polystyrene	Sulfhydryl	0.3-1.2	50-60	--	1-13	1,400 meq/1 Ag
Amberlite IRC-718	2	Crosslinked Polystyrene	Aminodiacetic Acid (Sodium Salt)	0.50	69	1.14	2-14	1.0 meq/ml
Amberlite IRC-505	2	Methacrylic Acid Divinyl Benzene	Methacrylic Acid	0.40	48	1.25	5-14	3.5 meq/ml CaCO$_3$
Amberlite IRC-84	2	Acrylic Acid Divinyl Benzene	Acrylic Acid	0.42	43	1.19	4-14	4.0 meq/ml CaCO$_3$

1 = Duolite International, Inc.
Diamond Shamrock Corporation
Cleveland, OH

2 = Rohm & Haas
Philadelphia, PA

Anionic exchangers are illustrated by resins which contain $-N^+H_3$ (weak base), $-N^+(CH_3)_3$ (strong quaternary, ammonium base) $-P^+-$ (strong phosphonium base). Moreover, aliphatic polyamines are more basic than amino groups attached to benzene rings. The most commercially important anion exchangers are produced by pearl (suspension) polymerization of cross-linked polystyrene. Basic groups are then introduced by chloromethylation of the polystyrene, followed by treatment with ammonia or amines. Ion-exchange resins are also produced by bulk-polymerization and grinding.

Ion-exchange resins for most applications are small particles, 0.1-mm to 1.0-mm diameter. The pore structure in ion-exchange resins is important since the pores must be open to allow uninterrupted diffusion paths across the medium. Macroporous, or "macroreticular" resins are composed of highly porous, rigid structures with macroscopic pores. They are normally prepared via pearl polymerization employing an organic solvent which is a "good" solvent for monomer, but a "poor" solvent for polymer. Leaching of the solvent by the water and/or evaporation leads to the formation of pores which are several hundred Angstroms in diameter.[27] Microreticular resins are gel-like with flexible hydrocarbon chains as the framework and do not contain any true porosity. The apparent porosity, or the intermolecular distances which limit the size of the ion that can migrate through the gel, is of the order of 40 Angstrom Units for low cross-linked, gel-type resins.[1]

The ion-exchange resins selected for this screening investigation included Duolite macroporous resins provided by Duolite International, Inc., Diamond Shamrock Corporation, and Rohm and Haas' Macroreticular Amberlite and Gel-Type Amberlite ion-exchange resins.

---

[27]Helfferich, Friedrich, Ion Exchange, McGraw Hill Co., Inc. 1962.

[1]Amberlite Ion Exchange Resins, Fluid Process Chemicals and Apparatus, Summary Chart of Typical Properties and Applications, Rohm & Haas Col., Phil., Pa., IE-241/78/81/83, July 1983.

The rate-determining step in ion exchange is the diffusion of the counter ions rather than an actual chemical exchange reaction at the fixed ionic groups. Hence, the reaction rate constants for the ion exchanger have little in common with rate constants of actual chemical reactions. Ion-exchange rates are complex and involve the individual diffusion rates of counter ions, concentration of fixed ionic groups, solution concentration, selectivity, particle size of resin, and film thickness. These are further complicated by the requirement to preserve electroneutrality. The latter is accomplished by interim build-up of space charge which slows down the faster moving counter ions in favor of the slower moving ions (Helfferich, et al., 1962).

A sponge model has been proposed which pictures the swollen ion-exchange resin as a heterogeneous system consisting of an inert matrix and pore liquid. Swelling is favored by factors such as solvent polarity; low degree of cross-linking; strong solvation tendency of fixed ionic groups; low valency, large and strongly solvated counter ions; and complete dissociation and low concentration of active components in pore liquid. Extremely high swelling pressures may develop upon expansion of the elastic matrix. The swelling pressure increases with increased degree of cross-linking for styrene-divinyl benzene (DVB) cationic ion exchangers, e.g., 200 atmospheres (10 % DVB) to 600 atmospheres (25 % DVB).

6.4.4 Laboratory Studies

6.4.4.1 Initial Screening Tests with Lead

More than thirty (30) commercial anionic and cationic exchange resins were initially investigated to determine their chemical reactivities with lead. Lead uptake by each resin from lead nitrate solution at pH=5 and retention of the lead following repeated washing of the swollen resin served as an indicator of the reaction. Both the exchange reaction and washing steps were conducted at pH=5, the lowest pH recommended for the EP Toxicity Test. Based on this preliminary

171

investigation, six (6) cationic exchange resins were chosen as the most promising for further study. A seventh, non-ionic resin, was included as a control. Table 35 lists the resins chosen and presents a brief description of the reactive functional group and the reaction product with lead.

6.4.4.1.1 Experimental Procedure

(a) The moisture content of each of the resins was determined on three one-gram aliquots taken from different locations in the container. The samples, in aluminum weighing dishes, were dried at 110°C ± 2°C for three hours, cooled to room temperature in a dessicator for ten minutes, and then reweighed to constant weight. The water content was calculated for each sample and averaged for the three aliquots. If individual determinations did not agree to with ± 2 %, the test was rerun. The dried samples were discarded after the test.

(b) Each resin underwent a rinse cycle before being used. Three grams of resin were weighed out and placed in a 50-mL Erlymeyer flask. Fifty mL of distilled, deionized water, pH controlled at 5, was poured into the flask. The flask was put on a shaker for 5 minutes and then allowed to settle for 10 minutes. The water was then filtered off. The resin was then considered ready for the introduction of a heavy metal. All equipment and glassware were cleaned and rinsed with distilled, deionized water prior to use.

(c) Three grams of resin were weighed out directly from the resin container and underwent a rinsing process as described in the previous section. The rinsed resin was introduced to 50 mL of $Pb(NO_3)_2$ solution calculated to have 0.8 g of $Pb(NO_3)_2$ or 0.5-g Pb per 50-mL H_2O. (The 50 mL of $Pb(NO_3)_2$ solution was actually taken from a 1-L stock solution made previously). The pH of the mixture was adjusted to 5 with a few drops of .1N NaOH. The mixture was then shaken for 20 minutes and allowed to settle for 10 minutes. The resin settled to the bottom. A 5-mL aliquot of the liquid was decanted for purposes of Atomic Absorption Spectroscopy (AAS) analysis. The new volume level was recorded. The 20-minute shaking, 10-minute settling, and the taking of a 5-mL aliquot was repeated. The sample was then filtered through a millipore vacuum-filter apparatus using an 0.45-μm membrane filter. The liquor was saved for AAS analysis. Fifty mL of distilled, deionized water, pH (=5) controlled, was poured over the resin remaining in the filter. The mixture was stirred with a stirring rod and allowed to settle for 20 minutes before vacuum was applied. The collected liquid was designated the "first" wash and saved for AAS analysis. The washing and filtering procedure was repeated. The collected liquid was designated "second" wash and saved for AAS analysis. Two additional washes were repeated and liquid aliquots were taken for Atomic Absorption analyses.

172

Table 35

ION-EXCHANGE RESINS REACTIVE WITH HEAVY METALS, e.g., Pb^{++}

Resin Identification	Supplier	Chemically Reactive Group	Group Name	Characteristic Reaction Product
Duolite CS-346	Diamond Shamrock	$R-C \overset{NOH}{\underset{NH_2}{\diagup}}$	Amidoxime	
Duolite ES-466	Diamond Shamrock	$R-CH_2-N \Big\langle \begin{smallmatrix} CH_2-C \diagup \!\! \diagdown \, ONa \\ CH_2-C \diagup \!\! \diagdown \, ONa \end{smallmatrix}$	Aminodiacetic acid (sodium salt)	
Duolite ES-467	Diamond Shamrock	$R-CH_2-NH-CH_2-\overset{O}{\underset{ONa}{P}}-ONa$	Amino phosphonic (sodium salt)	
Amberlite IRC-718	Rohm & Haas	Same as Duolite ES-466	Aminodiacetic Acid (Sodium Salt)	Same as Duolite ES-466
Amberlite IRC-50S	Rohm & Haas	$\overset{CH_3}{\underset{}{R}}-COOH$	Methacrylic Acid	$\overset{CH_3}{RCOO}-Pb-\overset{CH_3}{OOCR}$
Amberlite IRC-84	Rohm & Haas	$R-COOH$	Acrylic Acid	RCOOPbOOCR
Duolite ES-863 (Control)	Diamond Shamrock	(Non-Ionic, Functional Group Absent)		

173

6.4.4.1.2 Test Results: Initial Screening Measurements

Test results for the seven (7) ion-exchange resins, including one non-ionic resin control, are shown in Table 36. This table includes results of successive washes of the swollen, lead-containing resins, and compares the total quantity of lead removed to the quantity originally present (i.e., 7500-ppm Pb per gram of dry resin). It also displays the quantity of lead remaining in the resin and the quantity of lead retained in grams Pb/g resin. Best results were obtained with resins containing the chelating amino phosphonic (Duolite ES-467) and the aminodiacetic acid (Amberlite IRC-718, Duolite ES-466) groups. Amberlite IRC-505 (methacrylic acid group) and Amberlite IRC-84 (acrylic acid group) both showed poor retention of the lead. Surprisingly, the control ES-863 also showed good retention of the metal. This led to the next series of experiments, which are described in the following section.

6.4.4.2 Additional Screening Tests: Effects of (a) Increased Resin Presoak Time and (b) Drying Treated Resin Prior to Washing

6.4.4.2.1 Experimental Procedure/Test Results

Same procedure as previous except that (a) resins were presoaked, with shaking, for three days instead of 15 minutes and (b) the treated resin, after decant of the liquor, was dried for three hours at 40°C in a vacuum oven prior to washing. The results are shown in Tables 37 and 38, respectively.

It may be seen from these tables that the non-ionic control (ES-863) failed to adsorb lead under the modified resin treatment conditions. The effectiveness of the other resins was also reduced, but to a lesser degree by each of these treatments. The cationic exchange resins most effective for lead appear to be Duolite ES-467 and Amberlite IRC-718.

174

Table 36

ION EXCHANGE TESTS RESULTS WITH LEAD: INITIAL SCREENING MEASUREMENTS

Resin ID	Resin Weight (Dry), g	Free Lead in Liquor and Washes, ppm					Total Pb Extracted		Total Pb Remaining in Resin, g	Lead Reacted g Pb / g Resin	Other Comments
		Liquor	1st Wash	2nd Wash	3rd Wash	4th Wash	ppm	g			
Duolite ES-863	1.792	4100	520	40	.3	.7	4661	.2331	.1420	.0792	Control
Duolite CS-346	1.512	2600	1160	550	230	190	4730	.2365	.1385	.0916	
Duolite ES-467	.951	860	404	280	290	150	1984	.0992	.2758	.2900	
Duolite ES-466	1.185	3300	1080	340	280	75	5075	.2538	.1213	.1023	
Rohm & Haas IRC-718	1.485	150	140	140	49	10	480	.0245	.3506	.2361	
Rohm & Haas IRC-50S	1.086	6250	760	100	--	--	--	--	--	--	Aborted after 2nd Wash
Rohm & Haas IRC-84	1.695	6200	500	50	--	--	--	--	--	--	Aborted after 2nd Wash

Explanation:

Each test based on 3 g of wet resin as received from manufacturers
- A stock solution of Pb(NO3)2 containing 10 g of Pb per liter water was prepared. A filtered sample of this solution showed 7500 ppm (0.3750 g). Solution pH controlled at 5.
- Fifty ml of the above solution was used for each test.
- The solution in equilibrium with the resin is referred to as liquor.
- Fifty ml of distilled deionized water was used for each wash or a total of 200 ml of wash water per sample. Water pH controlled at 5.

175

Table 37

ION EXCHANGE TEST RESULTS WITH LEAD: EFFECT OF INCREASED RESIN PRESOAK TIME (A)

Resin ID	Resin Weight (Dry), g	Free Lead in Liquor and Washes, ppm					Total Pb Extracted		Total Pb Remaining in Resin, g	Lead Reacted g Pb / g Resin
		Liquor	1st Wash	2nd Wash	3rd Wash	4th Wash	ppm	g		
Duolite ES-863	1.8209	7300	220	30	4.4	1.9	7556	.3778	0	0
Duolite CS-346	1.5372	5000	940	455	275	180	6850	.3425	.0325	.0211
Duolite ES-467	.9669	2500	50	4.6	2.7	.4	2558	.1279	.2471	.2555
Duolite ES-466	1.5098	4000	1060	150	50	20	5280	.2640	.1110	.0735
Rohm & Haas IRC-718	1.1041	4600	100	.5	.2	<.2	4701	.2350	.1400	.1268

Explanation:

Each test based on 3 g of wet resin as received from manufacturers

- A stock solution of Pb(NO₃)₂ containing 10 g of Pb per liter water was prepared. A filtered sample of this solution showed 7500 ppm (0.3750 g). Solution pH controlled at 5.

- Fifty ml of the above solution was used for each test.

- The solution in equilibrium with the resin is referred to as liquor.

- Fifty ml of distilled deionized water was used for each wash or a total of 200 ml of wash water per sample. Water pH controlled at 5.

- In this series resin was soaked in distilled water for 3 days and rinsed before it was treated with lead solution.

176

Table 38

ION EXCHANGE TEST RESULTS WITH LEAD: EFFECT OF DRYING TREATED RESIN PRIOR TO WASHING (B)

| Resin ID | Resin Weight (Dry), g | Free Lead in Liquor and Washes, ppm | | | | | Total Pb Extracted | | Total Pb Remaining in Resin, g | Lead Reacted $\frac{g\ Pb}{g\ Resin}$ |
		Liquor	1st Wash	2nd Wash	3rd Wash	4th Wash	ppm	g		
Duolite ES-863	1.8209	7300	5.3	3.1	1.3	1.0	7311	.3655	.0095	.0052
Duolite CS-346	1.5372	5000	680	405	215	185	6485	.3243	.0508	.0330
Duolite ES-467	.9668	2500	55	50	40	11	2656	.1328	.2422	.2505
Duolite ES-466	1.5097	4000	1150	280	95	33	5558	.2779	.0971	.0643
Rohm & Haas	1.1041	4600	<.2	0	0	0	4600	.2300	.1450	.1313

Explanation:

Each test based on 3 g of wet resin as received from manufacturers

- A stock solution of Pb(NO₃)₂ containing 10 g of Pb per liter water was prepared. A filtered sample of this solution showed 7500 ppm (0.3750 g). Solution pH controlled at 5.
- Fifty ml of the above solution was used for each test.
- The solution in equilibrium with the resin is referred to as liquor.
- Fifty ml of distilled deionized water was used for each wash or a total of 200 ml of wash water per sample. Water pH controlled at 5.
- In this series the resin, after treatment with lead nitrate, was vacuum dried for 3 hours at 40°C prior to washing.

END

FILMED

DTIC
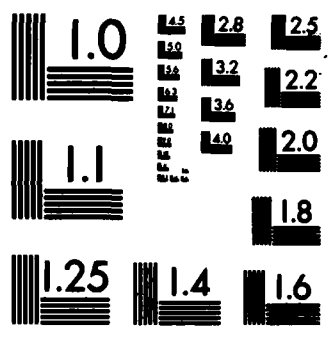
MICROCOPY RESOLUTION TEST CHART

NATIONAL BUREAU OF STANDARDS-1963-A

6.4.4.3 Additional Screening Tests: Effect of Increased Reaction Time

6.4.4.3.1 Experimental Procedure/Test Results

The experimental procedure described in 6.4.4.2.1(a) was compared with a modified procedure in which the reaction time between resin and lead nitrate solution was increased from approximately one hour [two successive periods of 20-minute shaking plus 10-minute settling, per 6.4.4.1.1(c)] to approximately 16 hours (includes additional overnight shake period added to the standard protocol). In addition, a new ion-exchange resin, Duolite GT-73, which contains sulfhydryl, SH, groups, was added to the two most promising resins, Duolite ES-467 and Amberlite IRC-718. Results are shown in Table 39, where it is seen that increasing the reaction time significantly improves the extent of reaction between the resin and the lead.

The modified procedure described above (16-hour reaction time) was applied to the two Duolite resins exhibiting intermediate reactivity with lead, CS-356 (Amidoxime group) and CS-466 (aminodracetic acid group), the non-ionic resin control ES-863, and two new Duolite resins:

ES-145 – Experimental resin with Isothiourea, $RCH_2SC \underset{NH}{\overset{NH_2}{\diagup}}$ functionality.[99]

ES-570 – Cross-linked phenol-formaldehyde resin with secondary amine functionality. In addition, the concentration of lead in solution was reduced to 1500 ppm.

---

[99]Warshawsky, A., Separation and Purification Methods, 9(2), 209-265, Marcel Dekker, Inc., 1980.

Table 39

ION EXCHANGE TEST RESULTS WITH LEAD: EFFECT OF REACTION TIME

Reaction Time* (Hours)	Resin ID	Resin Weight (Dry), g	Free Lead in Liquor and Washes, ppm					Total Pb Extracted		Total Pb Remaining in Resin, g	Lead Reacted g Pb / g Resin
			Liquor	1st Wash	2nd Wash	3rd Wash	4th Wash	ppm	g		
1	Duolite ES-467	.951	1300	130	3.0	0	0	1433	.072	.1284	.1350
	Amberlite IRC-718	1.086	1150	800	8.3	3.8	1.0	1963	.0982	.0018	.0017
	Duolite GT-73	1.02	5000	775	11.5	1.6	1.0	5789	.289	.0855	.0839
16	Duolite ES-467	.974	.25	.2	0	0	0	2.25	.0001	.2619	.2689
	Amberlite IRC-718	1.101	11	8	5	1.5	.3	25.8	.0013	.1237	.1124
	Duolite GT-73	1.02	210	11.5	.2	0	0	221.7	.0111	.1139	.1116

Explanation:

Each test based on 3 g of wet resin as received from manufacturers

- A stock solution of Pb(NO3)2 containing 10 g of Pb per liter water was prepared. A filtered sample of this solution showed 7500 ppm (0.3750 g). Solution pH controlled at 5.

- Fifty ml of the above solution was used for each test.

- The solution in equilibrium with the resin is referred to as liquor.

- Fifty ml of distilled deionized water was used for each wash or a total of 200 ml of wash water per sample. Water pH controlled at 5.

- In this series resin was soaked in distilled water for 3 days and rinsed before it was treated with lead solution.

- Filtered solution for 0125A contained 4000 lead (ppm)
  Filtered solution for 0125B contained 2000 lead (ppm)
  Filtered solution for 0125C contained 7500 lead (ppm)

  Filtered solution for 0126A contained 5250 lead (ppm)
  Filtered solution for 0126B contained 2500 lead (ppm)
  Filtered solution for 0126C contained 2500 lead (ppm)

*See Section e.4.4.3.1 for a more detailed description.

179

Results may be seen in Table 40: The non-ionic control shows no reaction, as expected; results for CS-346 and ES-466 are comparable with previous data and the two new resins do not appear to be reactive with lead.

6.4.4.4 Final Screening Tests: Optimum Procedure

6.4.4.4.1 Experimental Procedure/Test Results

All promising resins were retested with lead using an optimum procedure: Procedure 6.4.4.1.1 (in which the lead nitrate solution was maintained at 7500 ppm lead) modified to include presoaking the resin (6.4.4.2.1a) and extending the reaction time between resin and lead solution to 16 hours.

Results are found in Table 41, which includes tests with two additional Duolite resins:

A-464 - Macroporous cation exchange resin prepared from cross-linked polyacrylic acid. The weak acid resin was converted to the sodium form before use.

A-340 - Macroporous aliphatic epoxy - polyamine resin with tertiary amine functionality.

Excellent results were obtained with the new resins and improved performance was shown for resins previously tested.

6.4.5 Conclusions and Recommendations: Heavy Metal Sludges

Commercial ion-exchange resins have been shown to absorb and chemically react with large quantities of a lead nitrate simulant AAP sludge. Up to 35 parts, by weight, of lead per 100 parts of the dry resin have been taken up by a chemical reaction between the lead cation and specific functional groups in the resin. Non-ionic resins and

Table 40

ION EXCHANGE TEST RESULTS WITH LEAD:
EFFECT OF INCREASED REACTION TIME: LOW CONCENTRATION OF LEAD

Resin ID	Resin Weight (Dry), g	Free Lead in Liquor and Washes, ppm					Total Pb Extracted		Total Pb Remaining in Resin, g	Lead Reacted g Pb / g Resin
		Liquor	1st Wash	2nd Wash	3rd Wash	4th Wash	ppm	g		
Duolite ES-145	1	1150	130	5.0	1.8	0.8	1287	.064	.011	.011
Duolite ES-466	1	4.3	<.02	0	0	0	4.32	.0002	.0748	.0748
Duolite CS-346	1	50	120	70	24	22	286	.014	.061	.061
Duolite ES-863	1	1100	125	280	.5	.5	1506	.075	0	0
Duolite ES-570	1	590	95	21	17	16	739	.037	.038	.038

Explanation:

Each test based on 3 g of wet resin as received from manufacturers
- A stock solution of Pb(NO3)2 containing 10 g of Pb per liter water was prepared. A filtered sample of this solution showed 7500 ppm (0.3750 g). Solution pH controlled at 5.
- Fifty ml of the above solution was used for each test.
- The solution in equilibrium with the resin is referred to as liquor.
- Fifty ml of distilled deionized water was used for each wash or a total of 200 ml of wash water per sample. Water pH controlled at 5.
- Filtered Pb (NO3)2 solution contained 1500 ppm Pb (.075g) 16 hour reaction time (see Section 3.4.4.3.1).

181

Table 41

ION EXCHANGE TEST RESULTS WITH LEAD: OPTIMUM PROCEDURE

Resin ID	Resin Weight (Dry), g	Free Lead in Liquor and Washes, ppm					Total Pb Extracted		Total Pb Remaining in Resin, g	Lead Reacted g Pb / g Resin
		Liquor	1st Wash	2nd Wash	3rd Wash	4th Wash	ppm	g		
Duolite ES-467	1	75	285	210	165	135	870	.0435	.3315	.3315
Rohm & Haas IRC-718	1	120	265	123	50	35	593	.0297	.3454	.3454
Amberlite GT-73	1	4000	655	12	3.1	0.8	4671	.2335	.1415	.1415
Duolite ES-466	1	2300	1200	280	100	35	3915	.1958	.1793	.1793
Duolite CS-346	1	3200	1060	360	230	180	5030	.2515	.1235	.1235
Duolite C-464	1	1250	460	120	90	80	2000	.1000	.2750	.2750
Duolite A-340	1	1550	450	100	10.8	7.5	2118	.1059	.2691	.2691

Explanation:

Each test based on 3 g of wet resin as received from manufacturers

- A stock solution of Pb(NO3)2 containing 10 g of Pb per liter water was prepared. A filtered sample of this solution showed 7500 ppm (0.3750 g). Solution pH controlled at 5.
- Fifty ml of the above solution was used for each test.
- The solution in equilibrium with the resin is referred to as liquor.
- Fifty ml of distilled deionized water was used for each wash or a total of 200 ml of wash water per sample. Water pH controlled at 5.
- Filtered Pb(NO3)2 solution contained 7500 ppm Pb (0.375 g):16 hour reaction time (see Section e.4.4.3.1).

182

other resins which do not contain specific functional groups reactive with lead are not able to retain the metal on vigorous washing of the swollen resin with water.

Moreover, both the chemical reaction and washing steps have been conducted at pH=5 (the latter until the washings were relatively free of lead), the lowest pH recommended for the EP Toxicity Test where simple lead compounds, such as lead hydroxide, lead sulfide, lead carbonate, lead silicate, normally dissolve.

Optimum reaction conditions appear to be approached by thoroughly presoaking the resin prior to use and by allowing sufficient time for the reaction to occur.

Functional groups which exhibit the greatest reactivity with lead include, in descending order, aminodiacetic acid > amino phosphonic (sodium salt) > tertiary amine (in an epoxy-polyamine matrix) sulfhydryl > amidoxime.

Present costs for the ion-exchange resins investigated here range from under \$3/lb (C-26) to \$14/lb (CS-346). However, the high price of these materials may be offset by the potential benefits in lower shipping and storage costs presented by a low-volume, highly concentrated "ultimate sludge." Another intriguing possibility is the potential simplification of the wastewater treatment process for heavy metals at AAP plants by:

(a) Eliminating the neutralization, precipitation, coagulation, clarification and sludge formation steps and, instead,

(b) Utilizing a single resin-adsorption step in acid media to produce a low-volume, "chemically fixed" sludge and clean effluent discharge.

Another possibility to reduce the cost of these materials is for the resin manufacturer to produce a throw-away resin without the capability of regeneration or recycling, an important but cost-bearing property of present commercial ion-exchange resins.

It is recommended that further investigations be made of the effectiveness of ion-exchange-type resins with reactive functional groups for removal of other heavy metals such as chromium, cadmium, and zinc. Cost-benefit analyses should also be made by the Army on the use of ion-exchange resins for (a) producing stable, concentrated sludges for underground disposal in uncontrolled sites, and (b) simplifying the present wastewater treatment processes at AAP plants.

6.4.6 Laboratory Studies with TNT and RDX

Non-ionic adsorbent resins and weak base anionic resins are sold commercially for removing organic molecules from aqueous solutions. A number of the more promising commercial resins were selected for evaluation of their efficacy for removal of nitrobodies normally present in AAP pink water and sludges derived from these wastewaters. TNT and RDX, the major constituents of these wastewaters, served as the simulant sludges for carrying out these studies. Five (5) Duolite resins were tested: ES-570, A-7, S-761, ES-863, and C-26 (see Table 34 for properties). These were later narrowed down to resins A-7 and S-761, as described below.

6.4.6.1 Experimental Procedure

a. 100 g of each Duolite resins were washed with 100 mL of distilled deionized water. The last wash was with a spectrographic grade of water. The last wash was tested on a Perkin-Elmer Model 124 Double-Beam Grating Spectophotometer for UV absorption at 254 nm. The lowest background readings, 0.06 and 0.07 absorbance, were obtained for A-7 and S-761. Hence, these two non-ionic adsorbent resins were selected for the study.

b. Aliquots of the commercial-grade TNT and RDX explosives were taken from S-CUBED's Explosive Test Facility and set aside for this study. Impact sensitivity tests were performed on these materials and compared to a PETN (control) with the following results:

Explosive Material	Test Height (cm)	Results
TNT	100	Neg
RDX	40	Pos
PETN (Control)	35	Pos

Stock solutions of TNT and RDX were prepared in deionized, distilled water at 50 ppm and 20 ppm, respectively, and stored in the dark at $25°C \pm 5°C$ following the procedures recommended by M. Roth and E. A. Boyce[75]

c. The chemical analytical procedures employed to follow the resin take up of TNT and RDX from aqueous solutions were modeled after the methods described in References 75 and 9, except that liquid chromatography was not required since separate solutions of the two explosives were used. The Perkin-Elmer Model 124 Spectrophotometer, described above, was used to measure UV absorption.

The Perkin-Elmer spectrophotometer was calibrated for TNT using six aliquots representing 0.1 ppm, 0.5 ppm, 1.0 ppm, 2.5 ppm, 5.0 ppm and 50 ppm of TNT taken from the stock solution containing 50 ppm. The RDX calibration was accom-

---

[75]Roth, M. and E.A. Boyce, Continuous Monitoring of Pink Water from Carbon Adsorption Process, Technical Report ARLCD-TR-77047, April 1978.

[9]Bongiovanni, R, G.E. Podolak, et al., Analysis of Trace Amounts of Six Selected Polynitro Compounds in Soil, Am. Ind. Hyg. Assoc. J., 45 (4), 1984 (in press).

plished simularly by taking four aliquots from the RDX stock solution containing 20 ppm; namely, 1.0 ppm, 5.0 ppm, 10 ppm, and 20 ppm. All of the above aliquots were run against a blank containing GC spectrograde water. Resin blanks containing the resins under study, but without TNT or RDX, were also prepared. These blanks served as the background controls on the spectrophotometer for the actual experimental samples. The calibration curves for TNT and RDX appear as Figures 18 and 19, respectively.

d. The experimental procedures for these studies were similar to that described for the lead: One gram (dry basis) of each pre-washed, wet resin was shaken with 50 mL of the TNT solution and separately with 50 mL of the RDX solution for 24 hours, at which time adsorption was complete. No attempt was made to determine the minimum time to attain equilibrium adsorption. The wet resins were washed with deionized water, pH 5, until the washings were free of explosive using the analytical procedure (UV absorption) described above. Results are discussed in the next section.

6.4.6.2 Test Results

The test results are summarized in Tables 42, 43 and 44, where it may be seen that S-761 is more effective than A-7 in that the former has removed essentially all of the explosive from solution. The suggestive reaction between TNT and A-7 is of interest in view of the reaction noted earlier (Section 5.3.2.4) between nitrocellulose and polyamines.

PPM	ABS
0.1	0.045
0.5	0.08
1.0	0.125
2.5	0.22
5.0	0.385
50.0	1830.0

Calibration Samples

Absorbance at 254 mm
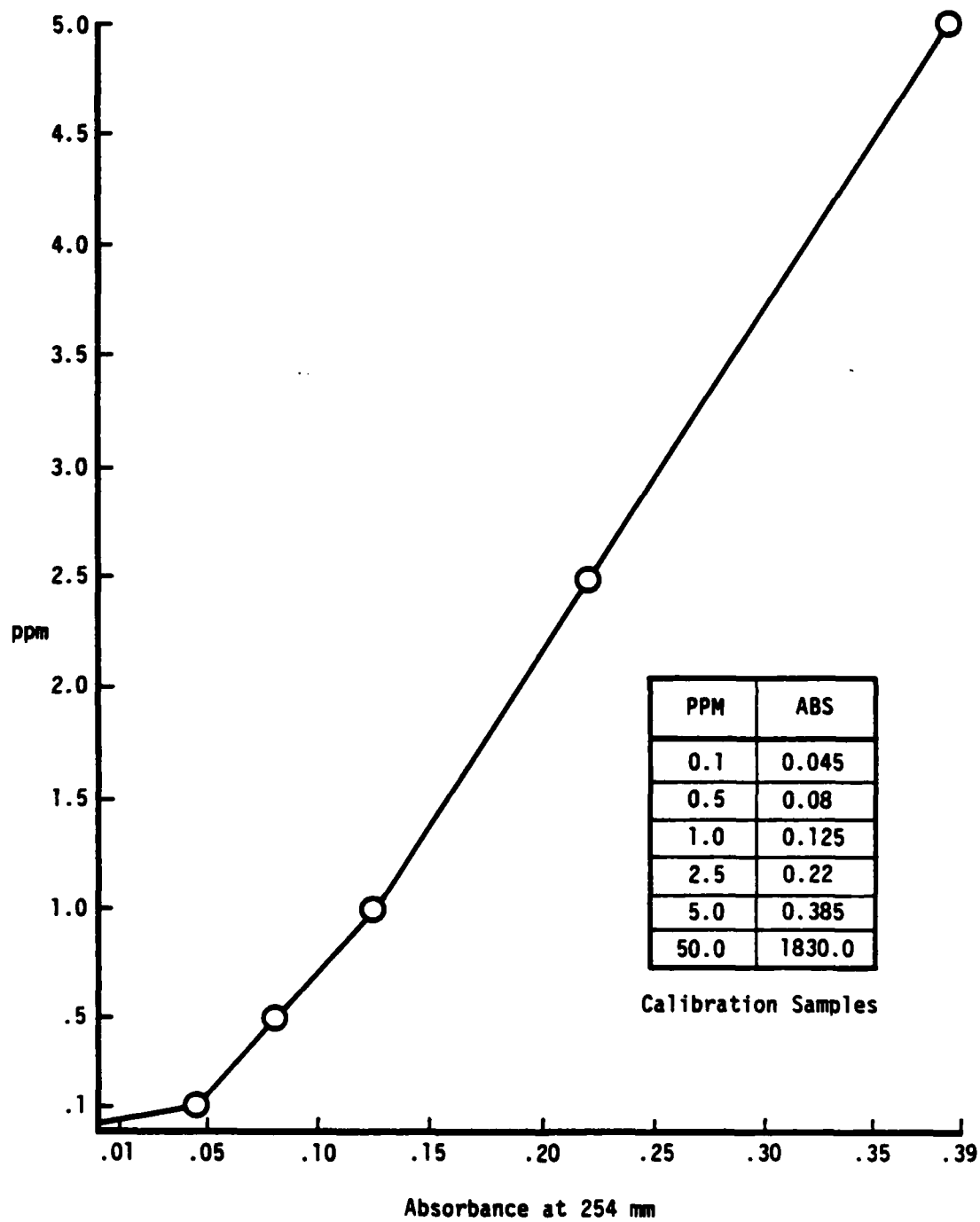
Figure 18.   Calibration Curve for TNT

PPM	ABS
1.0	0.05
5.0	0.08
10.0	0.105
20.0	0.16

Calibration Samples

Absorbance at 254 mm
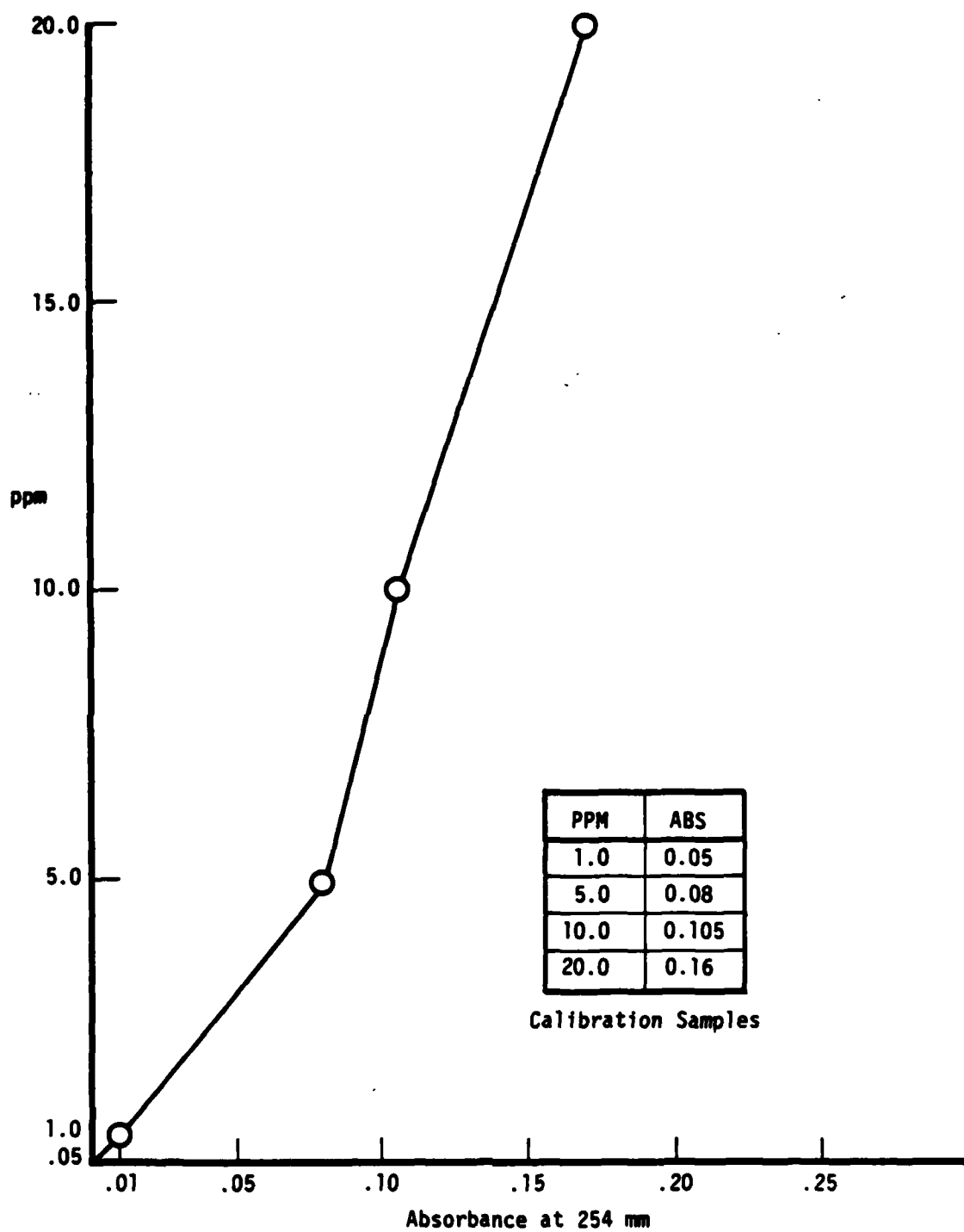
Figure 19. Calibration Curve for RDX

Table 42

ADSORPTION OF TNT BY NON-IONIC RESINS

Resin ID	Resin Weight (Dry), g	TNT in Liquor and Washes, ppm					Total TNT Extracted		Total TNT Remaining in Resin, g	TNT Absorbed g TNT g Resin	% Explosive Removed from 50 ml TNT Solution
		Liquor	1st Wash	2nd Wash	3rd Wash	4th Wash	ppm	g			
Duolite A-7	1	10	2.1	<0.1	0	0	12.2	.00061	.00189	.00189	75.6
Duolite S-761	1	1.8	0	0	0	0	1.8	.00009	.00241	.00241	96.4

TNT stock solution has 50 ppm of .0025 g TNT in 50 ml solution.

189

Table 43

ADSORPTION OF RDX BY NON-IONIC RESINS

Resin ID	Resin Weight (Dry), g	RDX in Liquor and Wash, ppm					Total RDX Extracted		Total RDX Remaining in Resin, g	RDX Adsorbed g, RDX / g Resin	% Explosive Removed from 50 ml RDX Solution
		Liquor	1st Wash	2nd Wash	3rd Wash	4th Wash	ppm	g			
Duolite A-7	1	6.8	0	0	0	0	6.8	.00034	.00066	.00066	66.0
Duolite S-761	1	1.0	0	0	0	0	1.0	.00005	.00095	.00095	95.0

RDX stock solution has 20 ppm of .001 g RDX in 50 ml solution.

190

Table 44

ADSORPTION OF TNT AND RDX BY NON-IONIC RESINS

Resin	Type	Functional Group	% Explosive Removed From 50-ml Explosive Solution	
			TNT[1]	RDX[2]
Duolite S-761	Cross-linked phenol-formaldehyde	Phenolic & methylol	96	95
Duolite A-7	Cross-linked phenol-formaldehyde	Secondary amine	76[3]	66

[1]50 ml of 50 ppm solution.

[2]50 ml of 20 ppm solution.

[3]Color change following adsorption suggestive of chemical reaction.

191

6.4.7 Conclusions and Recommendations: TNT and RDX

Two commercial non-ionic resins have been shown to effectively remove from solution and retain TNT and RDX at the lowest pH ($=5$) recommended for the EP Toxicity Test. Moreover, the result with resin A-7 and TNT suggests the possible formation of a reaction product between the two. Further work is necessary to determine whether the reaction product is more stable, i.e., desensitized, compared to the original explosive material.

It is recommended, as in the case of fixation of heavy metals with ion-exchange resins, that further investigation be made of the effectiveness of non-ionic resins for fixing (and possible desensitizing) explosive wastes from AAP plants. Cost-benefit analyses are warranted to compare, for example, incineration processes with open burning in combination with in-situ mixing with disposable reactive resins.

7.0 CONCLUSIONS AND RECOMMENDATIONS

Synthetic AAP sludges containing either inorganic or organic toxicants were encapsulated/fixed on a laboratory scale with selected E/F materials, including polysilicates, epoxides, polysulfides, commercial ion-exchange and non-ionic resins. Emphasis was placed on fixatives which were (a) capable of reacting and forming chemical and/or physical bonds with the contaminants, (b) low in cost, (c) readily available, (d) easy to process, and (e) expected to provide good physical properties.

7.1 POLYSILICATE FIXATIVES

Calcium polysilicate alone and/or admixed with Portland cement and fly ash was examined in some detail because these materials are used quite extensively to fix hazardous wastes. The studies conducted here indicated, contrary to reports in the literature, that "chemical" fixation of heavy metals such as lead, cadmium, and chromium by the calcium silicate probably does not occur. Promising results in the EP Toxicity Test are believed to be a consequence of the high alkalinity of these fixatives which rapidly neutralize the acetic acid leaching solution to produce final solution pHs of 10.7 and higher. Moreover, Portland cement and fly ash impart a buffering action which helps to maintain the high pH during the leaching. The high pH and buffering tend to retain the heavy metals in their insoluble carbonate/hydroxide/silicate forms. The absence of true chemical fixation of the metal into a three-dimensional lattice was confirmed by identical EP Toxicity Test results for either the cured or uncured sludge-fixative mixtures. Furthermore, IR, SEM, EDX, and XRD measurements of calcium polysilicate-treated AAP sludges containing lead did <u>not</u> reveal the formation of new compounds or crystalline structures indicative of chemical fixation.

Polysilicates also did not appear to react chemically with synthetic AAP sludges containing NC. However, the high alkalinity of

193

the sludge-fixative mixtures appeared to promote a denitration of the NC, as evidenced by the presence of nitrate in the leachate from the EP Toxicity Test. Additional studies are warranted to determine whether the apparent degradation of NC by the fixative is beneficial from an environmental viewpoint.

Studies with strongly alkaline, buffered, cementitious, siliceous fixed-AAP sludges containing heavy metals showed that it was possible to convert the metals into stable insoluble hydroxides/carbonates/ silicates which were highly resistant to leaching with acetic acid. In order to predict the useful life of these materials in the soil, a computer program (GEOCHEM) was investigated for calculating the speciation of the chemical elements in a soil solution containing the fixed sludge. In addition, laboratory tests with simple lead systems were carried out to validate GEOCHEM's predictions.

In one series of tests, the experimental data followed the pattern predicted by GEOCHEM in that the concentration of soluble lead was relatively constant under basic conditions, was lowest at the highest pH (10.8), and increased dramatically at pH between 6 to 8. Difficulties associated with sampling the gel and soluble phases, and the absence in the GEOCHEM data file of thermodynamic data for all possible chemical species, limited the success of this study. However, a computerized approach, such as GEOCHEM, does hold promise and may offer a means for estimating and predicting the environmental availability of different metal species present in AAP sludges fixed with cementitious materials.

7.2   EPOXIDE FIXATIVES

Amine-cured epoxides were tested as fixatives for organic contaminants such as NC because of anticipated stabilization via solubilization and formation of hydrogen-bonded structures. Instead, it was discovered that NC is both soluble and reactive in

194

diethylenetriamine, the curative agent for the epoxides investigated here. The reaction was vigorous when dry NC fines (produced at RAAP) were used. Compositions containing up to 15 weight percent NC and 66 weight percent solids loading were prepared successfully and tested. Infrared spectroscopy measurements of mixtures of NC in DETA were strongly indicative of the formation of a reaction product between these two materials. These findings suggested the possibility of decontaminating sludges containing NC by reacting and curing with amine-cured epoxide fixatives, providing that the reaction could be controlled and rapid heat rises (exotherms) were avoided. Additional studies are recommended in order the pursue further these promising results.

7.3 POLYSULFIDE FIXATIVES

Sodium polysulfide solutions were used successfully to isolate toxic heavy metals (lead, cadmium, chromium) from synthetic AAP sludges. The heavy metal polysulfides were readily consolidated with both epoxides and sulfurous materials to form monolithic structures with solids loadings (contaminant and fillers) up to 75 weight percent. Polysulfide treatment of heavy metals was also evaluated for simultaneous wastewater treatment and sludge fixation, as part of a total system concept. The expected waste volume reduction would result in considerable cost savings for materials, transportation and disposal. For example, material costs, on a "per-pound-of-toxicant (lead)-fixed basis," were estimated to be 16.6 times greater for cementitious fixatives than for polysulfide/epoxide fixatives; transport and disposal costs for a cementitious-fixed, LSAAP-type sludge were estimated to be ten times greater than for the corresponding epoxy-polysulfide fixed material. Furthermore, the polysulfide-epoxy fixed products exhibited superior mechanical properties (qualitative) and performance in the EP Toxicity Test.

X-ray diffraction measurements of the individual polysulfides prepared from Cr^{+3}, Cd^{+2}, and Pb^{+2} did not reveal salt-like

structures. However, the possibility exists that microcrystalline or
amorphous phases may have been present. Unexplained peaks were
observed in the chromium polysulfide and a larger crystallite size was
observed for lead polysulfide compared to a lead monosulfide control.

In view of the promising results with polysulfide/epoxide
fixatives, and the potential advantages of lower costs, small sludge
volumes and application to wastewater treatment processes, additional
studies of these materials are warranted.

7.4 FIXATION OF AAP ASH RESIDUES

A limited investigation was carried out to test the efficacy of
the polysulfide/polyepoxide fixative (which was developed for sludges)
for NG "slumps" ash received from RAAP and containing lead
contamination. A miniaturized leaching test was devised to simulate
the EP Toxicity Test because of the small quantity of ash that was
available. Leaching conditions were adjusted to pH 5, however, in
order to avoid secondary effects such as high alkalinity, buffering, or
factors which could influence (improve) the test results. Improved
performance was noted for the polysulfide-fixed and
polysulfide/polyepoxide-fixed ash compared to ash controls containing
no polysulfide. Additional studies are recommended using larger
quantities of ash to allow standard EP Toxicity testing. Cost-benefit
analysis of this procedure are also warranted.

7.5 ION-EXCHANGE RESIN FIXATIVES

A number of commercial ion-exchange resins containing chemically
reactive pendant groups were investigated as fixatives for simulant AAP
sludges containing lead contaminants. The resins selected were
primarily copolymers of styrene and divinyl benzene, with the specific
functional groups incorporated in the polymer structure. Both cationic
and anionic exchangers were tested. Best results were obtained by
first presoaking the resin with water and extending the reaction time

between resin and simulant sludge to 16 hours. Up to 35 parts, by weight, of lead per 100 parts of dry resin were taken up by the more chemically reactive resins, despite vigorous washing of the reaction product at pH=5 following the absorption step. Non-ionic resins and other resins which did not contain the specific reactive functional groups either did not react with lead or were unable to retain the metal on vigorous washing with water.

Best results were obtained with resins containing the following reactive groups, in descending order, aminodiacetic acid > amino phosphonic acid (sodium salt) > tertiary amine > sulfhydryl > amidoxime groups. The present high costs for these materials ($3 to $14 per lb) may be offset by cost-benefits associated with lower sludge volumes and lower shipping and storage costs. A possibility worthy of further study is the application of these materials to wastewater treatment in which a single resin absorption step is used to replace the present cumbersome and costly operations of neutralization/precipitation/coagulation/clarification/sludge formation and separate sludge treatment.

Commercial non-ionic resins, similarly, were found to effectively remove TNT and RDX from synthetic sludges containing these organic contaminants. Another potential benefit that should be investigated further is the finding that these organic contaminants may be desensitized by chemically reacting with the absorbant resin.

Finally, it is conceivable that a large market potential for ion-exchange and non-ionic resins as fixatives for AAP (and commercial) wastes would encourage manufacturers of these materials to produce low-cost, throw-away resins for this specific application.

8.0 REFERENCES

1. Amberlite Ion Exchange Resins, Fluid Process Chemicals and Apparatus, Summary Chart of Typical Properties and Applications, Rohm & Haas Col., Phil., Pa., IE-241/78/81/83, July 1983.

2. Anal. Chem. 32 (4) 495 (1960).

3. Anderson, Marc A., Robert K. Ham, Ranier Stegmann, Robert Stanforth, Robert Pojasek, ed., Toxic and Hazardous Disposal, Volume 2, Ann Arbor Science, 1982, pp. 145-168.

4. Arntson, R.H., F.W. Dickson, G. Tunell, "Systems S-Na$_2$O-H$_2$O and S-H$_2$O: Application to the Mode of Origin of Natural Alkaline Polysulfide and Thiosulfate Solutions," American Journal of Science, Vol. 258, October 1960, pp. 574-582.

5. Barney, G.S., "Fixation of Radioactive Waste by Hydrothermal Reactions with Clays," Prepared for U.S. Atomic Energy Commission by Atlantic Richfield Hanford Co., January 1974, 31 pp.

6. Bartos, M.T. and Polermo, M.R., "Physical and Engineering Properties of Hazardous Industrial Wastes and Sludges, EPA-600/2-77-139, September 1977.

7. Bell, N.E., Halverson, M.A., Mercer, B.M., "Solidification of Low-Volume Power Plant Sludges," CS-2171, Research Project 1260-20, Battelle Northwest Laboratories, December 1981.

8. Bender, E.S., Robinson, E.F., Moore, M.W., Thornton, W.D. and Asaki, A.E., "Preliminary Environmental Survey of Holston Army Ammunition Plant, Kingsport, Tennessee," Army Armament Research and Development Command, Aberdeen Proving Ground, MD, Chemical Systems Laboratory, EO-TR-77001, April 1976.

9. Bongiovanni, R, G.E. Podolak, et al., Analysis of Trace Amounts of Six Selected Polynitro Compounds in Soil, Am. Ind. Hyg. Assoc. J., 45 (4), 1984 (in press).

10. Brochure on Chemical and Physical Properties of Nitrocellulose, Hercules, Inc., Wilmington, Delaware.

11. Chamot, E.M. and C.W. Mason, Handbook of Chemical Microscopy, Vol. 1, 4th Edition, Wiley Interscience, New York, NY, 1983.

12. Chemical Week, "Rebuilding the Market for Highway Repair - A Role for Sulfur," Chemical Week, Vol. 131, No. 22, pp. 55, December 1, 1982.

13. Cheremisinoff, P. and R. Young, <u>Pollution Engineering Practice Handbook</u>, Ann Arbor Science, 1981.

14. Cleary, J.G., "NPDES Best Management Practices Guidance Document," Hydroscience, Inc., Knoxville, TN, EPA-600/9-79-045, December 1979.

15. Conners, J.R., "Ultimate Disposal of Liquid Wastes by Chemical Fixation," <u>29th Annual Purdue Industrial Waste Conference</u>, Purdue University, West Lafayette, IN, May 7, 1974, p. 906.

16. Digestion in Paar Bomb with Fuming Nitric Acid Followed by Hydrofluoric Acid Per <u>Anal. Chem.</u>, 45, 611 (1973).

17. Duvel, Jr., W.A., Gallagher, W.R., Knight, R.G., Kolance, J.R., McRalen, R.J., "State-of-the-Art of FGD Sludge Fixation," Final Report, EPRI-FP-671, January 1978.

18. EPP, Private Communication

19. Forsten, I., "Pollution Abatement in a Munitions Plant," <u>Environmental Science and Technology</u>, Vol. 7, No. 9, pp. 806-810, September 1973.

20. Fung, R., "Protective Barriers for Containment of Toxic Materials," Pollution Technology Review No. 67, Noyes Data Corp., 288 pp., 1980.

21. Glowacki, A.S. and MacDonald, D.C., "Protective Coatings for Application in Submersible Vessels, AD-460-364, 1965.

22. Goldstein, J.I. and Yakowitz, H., <u>Practical Scanning Electron Microscopy: Electron and Ion Microprobe Analysis</u>, Plenum Press, New York, pp. 95-147, 1975.

23. Goldstein, J.I. and Yakowitz, H., <u>Practical Scanning Electron Microscopy: Electron and Ion Microprobe Analysis</u>," Plenum Press, New York, pp. 213-217, 1975.

24. Griffiths, P.R., <u>Chemical Infrared Fourier Transform Spectroscopy</u>, John Wiley and Sons, New York, 1975, pp. 137-147.

25. Gustafsson, L. and A. Teder, <u>Thermal Decomposition of Aqueous Polysulfide Solutions</u>, Swensk Pappaerstidning Org, 72, p. 249, May 1969.

26. Hattori, M., Yaku, K, Nagaya, K., "Sludge Containing Chromium and Calcium by Heating with Silica," <u>Environmental Science and Technology</u>, Vol. 12, No. 13, pp. 1431-1434, 1978.

27.   Helfferich, Friedrich, Ion Exchange, McGraw Hill Co., Inc. 1962.

28.   Hercules Incorporated, "Disposal of Wastewater Treatment Sludges," Project PE-612, Phase I, FY'79, DO 48, Work Unit No. W-48, letter dated March 24, 1980, Hercules Incorporated, RAAP, Radford, VA.

29.   Ingle, S.E., M.D. Schuldt, and D.W. Schults, A User's Guide for REDEQL, EPA, U.S. Environ. Prot. Agency Rpt. EPA-600/3-78-024, Corvallis, Oregon, NTIS PB 280 149, 1978.

30.   Inorganic Chemistry, Vol. 8, No. 3, P. 566, March 1969.

31.   Janz, G.J., Technical Progress Report, Thermophysical Properties of Inorganic Polysulfides, Department of Energy, Contract DE-AC02-79R10387, December 1979.

32.   Jeffus, M. and Kerr, R. "Manual of Practice: The Disposal of Combined Municipal/Industrial Wastewater Residues (Metals)," EPA 600/2-79-052, February 1979.

33.   Jones, L.W., Malone, P.G., Thompson, D.W., Meyers, T.E., Chemical Fixation of Hazardous Industrial Wastes, U.S. Army Waterways Experiment Station, Vicksburg, MS, presented at American Institute of Chemical Engineers 71st Annual Meeting, November 1978.

34.   Jones, L.W., Malone, P.G., Meyers, T.E., Field Investigation of Contamination Loss from Chemically Stabilized Sludges, US Army Waterways Experiment Station, Vicksburg, MS, presented at the Sixth Annual Symposium on Treatment and Disposal of Hazardous Waste, EPA-600/9-80-010, March 1980.

35.   Josephson, J., "Immobilization and Leachability of Hazardous Wastes," Environmental Science and Technology, Vol. 16, No. 4, pp. 219-223, 1982.

36.   Klein, J., USATHAMA, Personal Communication, October 1982.

37.   Kurtzel, R.B. and Certulo, C., "The Effect of Environmental Pollutants on Human Reproduction, Including Birth Defects," Environmental Science and Technology, Vol. 15, No. 6, pp. 626-640, 1981.

38.   Landreth, R.E. and Mahloch, J.L., "Chemical Fixation of Wastes," Industrial Waste Engineering, pp. 16-19, July/August 1977.

39.   Leggett, D.J., Machine Computation of Equilibrium Concentrations -- Some Practical Considerations, Talanta 24:535-542, 1977.

40. Lubowitz, H. and Wiles, C., Management of Hazardous Waste by Unique Encapsulation Processes, presented at the 7th Annual Research Symposium on Land Disposal of Municipal and Hazardous Waste and Recovery, EPA, Philadelphia, PA, March 1981.

41. Ludwig, A.C., "Plasticized Sulfur Asphalt Replacements," Ind. Eng. Chem. Prod. Res. Div., 21, pp. 76-79, 1982.

42. Mahloch, J.L., "Leachability and Physical Properties of Chemically Stabilized Hazardous Wastes," Environmental Effects Laboratory, U.S. Army Engineer Waterways Experiment Stations, Vicksburg, MS, February 1976.

43. Mahloch, J.L., Averett, D.E., Bartos, Jr., M.J., "Pollutant Potential of Raw and Chemically Fixed Hazardous Industrial Wastes and Flue Gas Desulfurization Sludges," EPA-600/2-76-182, July 1976.

44. Malone, P.G., Mercer, R.B., Thompson, D.W., The Effectiveness of Fixation Techniques in Preventing the Loss of Contaminants from Electroplating Wastes, First Annual Conference on Advance Pollution Control for the Metal Finishing Industry, Lake Buena Vista, FL, January 17-19, 1978, EPA-600/8-78-010, May 1978.

45. Malone, P.G., Jones, L.W., Shafter, R.A., and Larson, R.J., Estimation of Pollution Potential of Industrial Waste from Small-Scale-Column Leaching Studies, presented at the Seventh Annual Research Symposium on Land Disposal of Municipal Solid and Hazardous Waste and Resource Recovery, March 16-18, 1981, Philadelphia, PA.

46. Malone, P.G. and Larson, R.J., Scientific Basis of Hazardous Waste Immobilization, ASTM D-34, Second Annual Symposium on Testing of Hazardous and Industrial Solid Waste (Poster Session), Lake Buena Vista, FL, January 1982.

47. Malone, P.G. and Francinques N.R., Solidification/Stabilization as a Technique for Treating Hazardous Wastes, Water Supply and Waste Treatment Group, Environmental Engineering Division, Environmental Laboratory, U.S. Army Engineering Waterways Experiment Station, Vicksburg, MS, prepared for the 24th Annual Meeting of the Mississippi Water Pollution Control Association, April 23-24, 1981, Jackson, MS.

48. Malone, P.G. and Meyers, T.E., Stabilization/Solidification of Waste from Uncontrolled Disposal Sites, presented at the EPA National Conference on Management of Uncontrolled Hazardous Waste Sites, Washington, D.C., October 1980.

49. Matthern, R., personal communication concerning U.S. Army Ammunition Plant Sludge Disposal Problems, November 10, 1982.

50. McDuff, R.E., and F.M.M. Morel, Description and Use of the Chemical Equilibrium Program REDEQL2, Tech. Rpt. EQ-73-02, Calif. Inst. Tech., Pasadena, California, 1973.

51. Method 353.2, EPA-600/4-79-020, 1979.

52. Meyers, T.E., Francinques, N.R., Thompson, D.E., Malone, P.G., Chemically Stabilized Industrial Wastes in a Sanitary Landfill Environment, U.S. Army Engineering Waterways Experiment Station, presented at the Sixth Annual Symposium on Treatment and Disposal of Hazardous Waste, EPA-600/9-80-010, March 1980.

53. Mercer, R.B., Malone, P.G., Broughton, J.D., "Field Evaluation of Chemically Stabilized Sludges," U.S. Army Engineering Waterways Experiment Station, Vicksburg, MS, EPA-600/9-78-016, pp. 357-365, September 1978.

54. Military Standard Method T209.10, 1 Sept. 1980.

55. Morel, F., R.E. McDuff, and J.J. Morgan, Interactions and Chemostasis in Aquatic Chemical Systems: Role of pH, pE, Solubility, and Complexation, In P.C. Singer (ed.), Trace Metals and Metal-organic Interactions in Natural Waters, Ann Arbor Science, Ann Arbor, Michigan, pp. 157-200, 1973.

56. Morel, F.M., and J.G. Yeasted. On the Interfacing of Chemical, Physical, and Biological Water Quality Models. In I.H. Suffet (ed.), Fate of Pollutants in the Air and Water Environments, Part 1. Adv. Environ. Sci. and Technol. 8:253-267, 1977.

57. Morel, F., and J. Morgan, A Numerical Method for Computing Equilibria in Aqueous Chemical Systems, Environ. Sci. Technol., 6:58-67, 1972.

58. National Academy of Sciences, National Academy of Engineering, Water Quality Criteria, 1972, "A Report of the Committee on Water Criteria," EPA-RF-73-033, U.S. Environmental Protection Agency, Washington, D.C., 594 pp., 1972.

59. Neal, L.G., "Army Munitions Plants Modernization Program Pollution Abatement Review," Final Report, Picatinny Arsenal, Dover, NJ, Contract No. DAAA21-72-C-0625, TRW, Redondo Beach, CA, August 1973.

60. Neely, N.S., Walsh, J.S., Gillespie, D.P., Schauf, F.J., Remedial Actions at Uncontrolled Hazardous Waste Sites, SCS Engineers, presented at the Seventh Annual Research Symposium on Land Disposal of Municipal Solid and Hazardous Waste Recovery, Philadelphia, Pennsylvania, March 1981.

61. Nickless, G., Inorganic Sulfur Chemistry, pg. 690, Elsevier
     Publishing Co., New York, 1968.

62. Patterson, J., Shapita, N.I., Brown, J., Duckert, W., Polson, J.,
     "State-of-the-Art Military Explosives and Propellants Production
     Industry," Vol. II, Wastewater Characterization Technical Report,
     The American Defense Preparedness Association, Industrial
     Environmental Research Laboratory, Cincinnati, OH,
     EPA-600/2-76-213C, 273 pp., August 1976.

63. Patterson, J., Shapita, N.I., Brown, J., Duckert, W., Polson, J.,
     "State-of-the-Art Military Explosives and Propellants Production
     Industry," Vol. III, Wastewater Characterization Technical
     Report, The American Defense Preparedness Association, Industrial
     Environmental Research Laboratory, Cincinnati, OH,
     EPA-600/2-76-213C, 181 pp., October 1976.

64. Perry, Robert H. and Chilton, C.H., Chemical Engineers' Handbook,
     5th Edition, McGraw Hill, 1973.

65. Pojasek, R.B., Toxic and Hazardous Waste Disposal, Vol I,
     Processes for Stabilization/Solidification, Ann Arbor Science,
     Inc., Ann Arbor, MI, 1979.

66. "Process Design Manual for Sludge Treatment and Disposal, EPA
     625/1-74-006, U.S. Environmental Protection Agency, pgs. 8-22 to
     8-26, October 1974.

67. Ribaudo, C., Campbell, C., Bulusu, S., Fisco, W, Chen, T.H., "The
     Chemical Characterization of Pollutants in Waste Water From
     Volunteer Army Ammunition Plant," US Army Armament Research and
     Development Command, Large Caliber Weapons Systems Laboratory,
     Dover, NJ, Technical Report ARLCD-TR-81028.

68. Robinson, J., "Chemical Fixation of Sludge," Day and Zimmermann,
     Inc., Lone Star Division, Texarkana, TX, 32 pp. (undated).

69. Robinson, J., "Chemical Fixation of Sludge: Laboratory Studies,"
     Contractor Report ARLCD-CR-82044, U.S. Army Research and
     Development Command, Large Caliber Weapon Systems Laboratory,
     Dover, New Jersey, AD-E400 903, October 1982.

70. Rosecrance, A.B. and Kulkarni, R.K., (Army Medical Bioengineering
     Research Development Laboratory, Fort Detrick, Frederick, MD),
     "Fixation of Tobyhanna Army Depot Electroplasting Waste Samples
     by Asphalt Encapsulation Process, USAM BRDL-TR-7902, January 1979.

71. Rosen, E. and R. Tegman, A Preparative and X-Ray Powder
     Diffraction Study of the Polysulfides Na_2S_4 and Na_2S_5,
     Acta Chemical Scandinavica, 25, 3329, 1971.

72. Ross, D., Inorganic Infrared and Raman Spectra, McGraw Hill Company, Ltd., London, 1972, pp. 95-112.

73. Roth, Howard; personal communication on January 28, 1983, PQ Corporation, "Silicate Research and Development Department," Lafayette Hill, PA.

74. Roth, M., "Non-Polluting Process for Desensitizing Explosives," AD D006421, 18 December 1978.

75. Roth, M. and E.A. Boyce, Continuous Monitoring of Pink Water from Carbon Adsorption Process, Technical Report ARLCD-TR-77047, April 1978.

76. Rousseaux, J.M., Craig, A.B., "Stabilization of Heavy Metal Wastes by the Soliroc Process," PB 81-191900, Proc. on Adv. Poll. Contr. for Metal Fin. Ind., Orlando, FL, April 1980, pp. 70-75.

77. Rysman de Lockerente, Serge, Van de Voorde, Norbert, "A Procedure for the Treatment of Waste By-Products," Letter of Patent, Report filed in support of, to the International Society of Advertising and Business Assoc./SIPAC, 1978. FR, Brevet D'Invention No. 831.427.

78. Salas, Robert K., Robert B. Pojasek, ed., Toxic and Hazardous Waste Disposal, Vol. I, Ann Arbor Science, 1929, pp. 321-348.

79. Sandmann, H., "Modern Methods of Effluent Treatment," Brown Boveri Review, Vol. 64, No. 3, pp. 174-179, March 1977.

80. Smith, D.F., Quantitative FT-IR Spectroscopy of Polymer Surfaces Using Variable Angle ATR, in Digilab Users Conference, June 1980, Digilab, Cambridge, Massachusetts.

81. Smith, L.L. and Dickenson, R.L.(Radford Army Ammunition Plant), and Pregren, E.R. (Picatinny Arsenal), "Engineering Study of Disposal Methods for Waste Acid Neutralization Sludge," TR 471, November 1973.

82. Smith, L.L. and Dickenson, R.L. (Radford Army Ammunition Plant, Hercules, Inc., Radford, VA), Casrazza, J.A. (Picatinny Arsenal), Propellant Plant Pollution Abatement - Engineering Investigation to Develop Optimum Control Measures to Prevent Water Pollution," TR 4818, March 1975.

83. Sodium Silicates, Hydrated and Anhydrous Powders Bulletin, 17-104/478, The PQ Corporation, pp 1-9, 1978.

84. Sposito, G and S.V. Mattigod, GEOCHEM: A Computer Program for the Calculation of Chemical Equilibrium in Soil Solutions and Other Natural Water Systems, University of California, Riverside, California, 1980 (Appendix).

85. Stevens, B.W. and McDonnel, R.P. (Rohm and Haas Company, Philadelphia, PA), Andren, R.K., Nystrom, J.M. (U.S. Army Natick Development Center, Natick, Massachusetts), Explosives Removal from Munitions Wastewaters, presented at the 30th Annual Purdue Industrial Waste Conference, May 6-8, 1975.

86. Swope, G. H. (Waste Management and Pollution Control), "Hazardous Waste Discussed at International Meeting of Chemical Societies, Industrial Wastes, Vol. 25, No. 5, pp. 26-28, August/September 1979.

87. Technical Bulletin SP-LS-7, Grades of Liquid Sodium Silicates, Diamond Shamrock Corporation, 1981.

88. Thomas, J.C. and Carotti, A., "How the Army Does a Bang-up Job of Treating Effluents," Environmental Science and Technology, Vol. 10, No. 8, pp. 751-756, August 1976.

89. Thompson, D.W., "Elutriate Test Evaluation of Chemically Stabilized Waste Materials," Environmental Laboratory, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS, EPA-600/2-79-154, September 1974.

90. Unit Operations for Treatment of Hazardous Industrial Wastes, Pollution Technology Review, No. 47, pg. 326 (Table 3), pg. 495 (Table 2), D. J. DeRenzo, Editor, Noyes Data Corporation, New Jersey, 1978.

91. U.S. Army Engineering Waterways Experiment Station, Environmental Laboratory, "Survey of Solidification/Stabilization Technology for Hazardous Wastes," Vicksburg, MS, EPA-600/2-79-056 (PB-299-206) July 1979.

92. U.S. Army Environmental Hygiene Agency, Chemical Fixation of Electroplating Wastes, Tobyhanna Army Depot, Tobyhanna, PA, July 25-29, 1977, Solid Waste Consultation, No. 26-0027-78, Department of Army, Aberdeen Proving Ground, MD, pp. 1-9.

93. U.S. Army Environmental Hygiene Agency, U.S. Department of the Army, Hazardous Waste Management Consultation No. 37-26-0150-81, Savanna Army Depot Activity, Savanna, IL, April 1981, Aberdeen Proving Ground (Internal Correspondence), August 1981.

94. U.S. Army Environmental Hygiene Agency, Hazardous Waste Special Study No. 37-26-0159-81, Ft. Stewart, GA, April 1981, U.S. Department of the Army, Aberdeen Proving Ground, MD (Internal correspondence), September 28, 1981.

95. U.S. Army Environmental Hygiene Agency, Sludge Disposal From Industrial Waste Treatment Plant, Watervliet Arsenal, Watervliet, NY, May 14-18, 1979, APAP Project No. D-1533-W, Hazardous Waste Special Study No. 81-26-8204-80, Department of the U.S. Army, Aberdeen Proving Ground, MD. pp. 1-10.

96. U.S. Army Research and Development Command, U.S. Department of the Army, Characterization and Disposal of Wastewater Treatment Sludges, DO-48, Work Unit W-48, Dover, NJ, letter dated January 6, 1981.

97. U.S. Department of the Army THAMA, Disposal of Wastewater Treatment Sludges (Overall Project Concept), 1981 Annual Symposium Submissions, W-48.

98. Wahl, R.M., "Electrolytic Disposal of Lead Sludges in an Acetate-Containing Electrolyte," Project No. 79269, TR 337, January 4, 1982, Mason & Hanger - Silas Mason Co., Inc., Iowa Army Ammunition Plant, Middletown, Iowa.

99. Warshawsky, A., Separation and Purification Methods, 9(2), 209-265, Marcel Dekker, Inc., 1980.

100. Webb, W.M., Control, Decontamination and Disposal of Mercury, Report OEHL-79-149, Brooks Air Force Base, November 1979.

101. Wheelock, T.D., "Disposal of RAAP Wastewater Treatment Sludges by Incineration," Phase I, Final Report, Chemical Engineering Department and Engineering Research Institute, Iowa State University, Ames, Iowa, April 30, 1982.

102. Wiegele, G.L. "The State-of-the-Art of Waste Disposal Technology," Consulting Engineer, Vol. 55, No. 3, pp. 99-102, September 1980.

9.0 GLOSSARY OF ABBREVIATIONS AND ACRONYMS

AAP	Army Ammunition Plant
AAS	Atomic Absorption Spectroscopy
AD	Army Depot
AEHA	Army Environmental Health Agency
APAP	Army Pollution Abatement Program
ATR	Attenuated Total Reflection
BOD	Biological Oxygen Demand
CFR	Code of Federal Regulations
COD	Chemical Oxygen Demand
DETA	Diethylenetriamine
DTIC	Defense Technical Information Center
DVB	Divinyl Benzene
E/F	Encapsulation/Fixation
EDX or EDAX	Energy-Dispersive X-ray Analysis
EP	Extraction Procedure
EPON 828	Diglycidyl Ether of Bisphenol A
FTIR	Fourier Transform Infrared Spectroscopy
GC	Gas Chromatography
GEOCHEM	Computer Program for calculating the equilibrium speciation of the chemical elements in a soil solution
HMX	Cyclotetramethylenetetranitramine
IR	Infrared Spectroscopy
LAP	Load, Assemble and Pack
LSAAP	Lone Star Army Ammunition Plant
MP FAB	Metal Parts Fabrication
N/A	Not Applicable
NC	Nitrocellulose
NG	Nitroglycerin
NPDES	National Pollutant Discharge Elimination System
NTIS	National Technical Information Service
PACT	Pollution Abatement and Environmental Control Technology
PCBs	Polychlorinated Biphenyls
PETN	Pentaerythrite Tetranitrate
pH	Negative logarithm to the base 10 of the hydrogen ion concentration
PPM	Parts Per Million
RAAP	Radford Army Ammunition Plant
RCRA	Resource Conservation Recovery Act
RDX	Cyclotrimethylenetrinitramine
RF-475	Neopentyl Glycol Diglycidyl Ether
SEM	Scanning Electron Microscope
TEM	Transmission Electron Microscope
TNT	Trinitrotoluene
TOC	Total Organic Carbon
TS	Total Solids
TSS	Total Suspended Solids
USEPA	US Environmental Protection Agency
WES	Waterways Experimental Station
WTS	Water Treatment System
XRD	X-ray Diffraction

207

DISTRIBUTION LIST

Department of the Army   1 copy
Office of the Chief of Engineers
ATTN: DAEN-RDM
Washington, D.C.   20314

Commander
U.S. Army Materiel Development and Readiness Command   1 copy
ATTN: DRCIS-A
5001 Eisenhower Avenue
Alexandria, Virginia   22333

Commander   8 copies
U.S. Army Toxic and Hazardous Materials Agency
ATTN: DRXTH-TE-D/Mr. R. Bartell
Aberdeen Proving Ground, Maryland   21010

Commander   1 copy
U.S. Army Munitions Production Base Modernization Agency
ATTN: DRSMC-PMB(D)
Dover, New Jersey   07801

Commander   1 copy
U.S. Army Environmental Hygiene Agency
ATTN: HSE-E
Aberdeen Proving Ground, Maryland   21010

Administrator   6 copies
Defense Technical Information Center
ATTN: DTIC-TC
Cameron Station
Alexandria, Virginia   22314

Commander   2 copies
U.S. Army Logistics Management
ATTN: DRXMC-MR-D
Fort Lee, Virginia   23801

APPENDIX A

SLUDGE COMPOSITION DATA

APPENDIX A.1

LSAAP SLUDGE COMPOSITE CHARACTERIZATION*

Parameter	Concentration (mg/1)**
Aluminum	26.2
Arsenic	0.001
Barium	9.4
Calcium	271
Cadmium	0.30
Chromium	8.8
Iron	5190
Lead	630
Manganese	22.8
Mercury	0.004
Selenium	0.029
Silver	0.01
Sodium	1060
Zinc	56
Total Solids	15455
Total Suspended Solids	12400
Volatile Solids	2315
Total Organic Carbon	120
Alkalinity	2371 as $CaCO_3$ at pH 3.7
Moisture	98.45%
n-Propylphthalate	10 ppm
pH	7.81 pH units

---

*Reference 68,69

**Except where otherwise noted.

APPENDIX A.2

CHARACTERIZATION OF LONE STAR AAP
WASTEWATER TREATMENT SLUDGES*

(mg/l)

SLUDGE COMPONENT	SLUDGE SLURRY**	SLUDGE ANALYSIS	EFFLUENT ANALYSIS
TS	15,455		
TSS	12,400		
CALCIUM	271	291	
IRON	5,190	5,108	
LEAD	630	657	0.14
SODIUM	1,060	1,183	
OTHER INORGANICS	154.2	154.8	0.22
AMMONIA-NITROGEN			4.7
COD			470.0

NOTE: ANALYSIS FOR TOC AND ORGANIC COMPONENTS HAVE NOT BEEN COMPLETED

---

* Reference 97

**Composite of 13 batches of sludge

CHARACTERIZATION OF RAAP
WASTEWATER TREATMENT SLUDGES*

QUANTITY PRODUCED, LB/DAY DRY WEIGHT

SLUDGE COMPONENT	NG-1 & ALCOHOL RECTIFICATION	NG-2	SAR	BIOLOGICAL	TOTAL
TOTAL SLUDGE (DRY WT)	3,564	4,915	37,749	1,080	47,308
CALCIUM SULFATE	--	423	35,144	--	35,567
CALCIUM HYDROXIDE	343	1,703	76	200	2,322
CALCIUM CARBONATE	1,422	2,262	--	--	3,684
NITROCELLULOSE	693	--	--	--	693
LEAD	2.5	1.5	--	--	4
IRON	12.5	7.9	38	--	58.4
OTHERS**	895	442	2,415	880	4,632
MAGNESIUM	31	37	38	--	106
SODIUM	32	19	--	--	51
INORGANIC NITRATES	109***	14	--	--	123
SILICA	18.5	5.5	38	--	62
CYANIDE	5.5***	--	--	--	5.5

---

* Reference 97

** Others also consisted of CO_2, organics, and bound H_2O based upon their volatility at 825°C

***Cyanides and nitrates are present in aged sludge only due to the decomposition of the nitrocellulose by the calcium hydroxide.

APPENDIX A.4

TOBYHANNA AD ELECTROPLATING WASTES*

WASTE GENERATED	METALS ANALYZED	CONCENTRATION OF METALS PRESENT (ppm)
Chrome Plating Waste	Chrome	2,750
	Copper	7,180
	Cadmium	110
	Lead	30
Copper Plating Waste	Chrome	420
	Copper	11,300
	Cadmium	4,170
	Lead	1,200
	Tin	100
Lead and Tin Plating Waste	Chrome	3
	Copper	1,300
	Cadmium	330
	Lead	1,500
	Tin	140

*References: 28, 92

APPENDIX A.5

SYNTHETIC SAMPLE NO. 1* FROM TOBYHANNA AD**

	mg/kg	METAL
Cadmium iodide	300	Cd^{+2}
Chromium chloride	800	Cr^{+3}
Chromium trioxide	1000	Cr^{+6}
Ferric nitrate	1400	Fe^{+3}
Lead acetate	6	Pb^{+2}
Nickel acetate	8	Ni^{+2}
Sodium cyanide	500	CN^{-1}
Zinc oxide	850	Zn^{+2}

* The sample was made to 1 kg by the addition of $CaSO_4$ (anhydrous).

** Reference: 70

APPENDIX A.6

SYNTHETIC SAMPLE NO. 2* FROM TOBYHANNA AD**

Chemical Compount	mg/kg of Metal	
Aluminum ammonium sulfate	1000	Al^{+3}
Barium chloride	1000	Ba^{+2}
Cadmium iodide	1000	Cd^{+2}
Chromium chloride	1000	Cr^{+3}
Chromium trioxide	1000	Cr^{+6}
Cupric chloride	1000	Ca^{+2}
Ferric nitrate	1000	Fe^{-3}
Lead acetate	1000	Pb^{+2}
Magnesium sulfate	1000	Mg^{+2}
Manganese chloride	1000	Mn^{+2}
Mercury chloride	1000	Hg^{+2}
Nickel acetate	1000	Ni^{+2}
Selenium (powder)	1000	Se
Silver sulfate	1000	Ag^{+1}
Sodium arsenate	1000	As^{+5}
Sodium cyanide	1000	CN^{-1}
Tin (powder)	1000	Sn
Zinc oxide	1000	Zn^{+2}

*   The sample was made to 1 kg by the addition of calcium sulfate (anhydrous).

** Reference: 70

APPENDIX A.7

AVERAGE ANALYSIS FOR SAVANNA AD LEAD AZIDE SLUDGE*†

Moisture	19.3%
Sodium Azide	35.2%
Sodium Hydroxide	2.2%
Sodium Carbonate	1.6%
Sodium Plumbite	0.7%
Unidentified Water-Soluble Material	3.5%
Lead Metal	5.2%
Insoluble Lead Compounds	32.3%

† The unidentified water-soluble material may be largely, if not entirely, sodium chloride.

*Tash, J.E. and Wahl, R.M., "Chemical Characterization of Sludge from Lead Azide Electrolysis," Project No. 82371, TR 343, January 29, 1982, Mason & Hanger - Silas Mason Co., Inc., Iowa Ammunition Plant, Middletown, Iowa.

APPENDIX B

ENGINEERING ASSUMPTIONS FOR COST ESTIMATES

SLUDGE MAKE-UP

Wet Sludge

For cementitious   98.45% water)

    fixative: 0.063%   )   LSAAP

Dry Sludge

For epoxy fixative: 10% Pb-P.S.
                                           65% inert solids (e.g., CaCO3)

For sulfur fixative: 10% Pb-P.S.
                                           50% inert solids

CONTAINMENT IN SLUDGE PRIOR TO E/F TREATMENT

	Polysulfide Epoxy	Polysulfide in Sulfur
$\dfrac{0.0063\ \text{Parts Pb}}{100\ \text{Parts Wet Sludge}}$	$\dfrac{0.00063\ \text{Parts Pb}}{1.54\ \text{Parts}}$ Dry Sludge	$\dfrac{0.00063\ \text{Parts Pb}}{1.54\ \text{Parts}}$ Dry Sludge
or	or	or
$\dfrac{630\ \text{Parts Pb}}{10^{8}\ \text{Parts Sludge}}$	$\dfrac{630\ \text{Parts Pb}}{1.54 \times 10^{6}\ \text{Parts}}$ Dry Sludge	$\dfrac{630\ \text{Parts Pb}}{1.54 \times 10^{6}\ \text{Parts}}$ Dry Sludge

CEMENTITIOUS

Weight fixative used (LSAAP) per one pound sludge.

$$\frac{170\#}{300\#} = \frac{0.57\#}{1\#}\ \frac{\text{Cement}}{\text{Sludge}}$$

Weight fixative used (LSAAP) per one pound lead.

$$\frac{170\#}{0.189\#\ \text{Pb}} = \frac{890\#}{1\#}\ \frac{\text{Cement}}{\text{Pb}}$$

FIXATIVE-TO-SLUDGE WEIGHT RATIOS

Cementitious/Sludge (Wet) - (LSAAP) $= \dfrac{170\#}{300\#} = 0.567$

Epoxy/Sludge (Dry) $= \dfrac{25\#}{75\#} = 0.33$

Epoxy/Sludge (Dry) $= \dfrac{40\#}{60\#} = 0.67$

FIXATIVE-TO-Pb WEIGHT RATIOS

Cementitious/Pb (LSAAP) $= \dfrac{170\#}{300\# \times 0.063\% \text{ Pb}} = \dfrac{890\# \text{ cement}}{1\# \text{ Pb}} = 890$

Epoxy/Pb $= \dfrac{25}{75} \times \dfrac{1}{\left(\dfrac{10 \text{ Pb-P.S.}}{75 \text{ Sludge}}\right)} \times \dfrac{1}{\left(\dfrac{0.62 \text{ Pb}}{1 \text{ Pb-P.S.}}\right)} = 4.0$

Sulfur/Pb $= \dfrac{40}{60} \times \dfrac{1}{\left(\dfrac{10 \text{ Pb-P.S.}}{60 \text{ Sludge}}\right)} \times \dfrac{1}{\left(\dfrac{0.62 \text{ Pb}}{\text{Pb-P.S.}}\right)} = 6.5$

UNIT COSTS OF FIXATIVES AND REAGENTS

Cementitious Treatment Chemicals = \$0.10/lb (LSAAP)
 (see Pages 9-10)   = \$0.00033/300 lb Sludge

Epoxy   = \$1.20/lb
Na_2S_4 = \$0.67/lb

Sulfur   = \$0.05/lb
Na_2S_4 = \$0.67/lb

PRECIPITATION, COAGULATION, FLOCCULATION COSTS (Raw Materials)*

Lime $ 400/yr
Coagulant Acid   970/yr   } **
H_2SO_4 160/yr   }
                 $1530/yr   or $0.736/day
                            or $0.736/82,000 gallons

NOTE: @ LSAAP 13 batches, 350 gallons each, are collected over ten weeks -- assume treatment is accomplished after ten week.

13 x 350 gals = 4550 gals, or 38,000#

∴ | Cost of Raw Treatment Chemicals $\approx \dfrac{\$0.736}{82,000 \text{ gals}}$ x 4550 gals = $0.42 |

Cost of Raw Treatment Chemicals = $\dfrac{\$0.042}{4550 \text{ gallons of sludge}}$

In fixation using cementitious materials (LSAAP) as

$\dfrac{170\# \text{ cement}}{300\# \text{ sludge}}$ requires the following treatment chemicals:

300# sludge x $\dfrac{\$0.042}{38,000\#}$ = | $\dfrac{\$0.00033}{300\# \text{ sludge}}$ |

*Unit operatings of Hazardous Industrial Wastes by J. Berkowitz, Noyes Data, 1978, p. 524.

**Based on "small" wastewater treatment process, 82,000 gallons per day.

APPENDIX C

BASIC INFORMATION ON LABORATORY PREPARATION OF SODIUM SILICATE

Calcium Chloride and Lead Nitrate Formulas

BASIC INFORMATION ON LABORATORY PREPARATION OF SODIUM SILICATE - CALCIUM CHLORIDE FORMULAS

MIX NO.	CHEMICAL INGREDIENTS (P.B.W.)							% Pb SOLIDS	pH	GEL/DRY. TIME	FINAL CONSISTENCY	MATERIAL APPEARANCE
	H2O	CaCl2	SS	Pb (NO3)2	LIME	P.C.	OTHER					
03090	60.9	0.45	4.5	--	39.2	--	--	1.0	NA	1 day/1 days	Crumbles under moderate pressure.	limestone
0310C	81.3	1.3	17.4	--	--	--	--	7.0	NA	NA/1 days	Hard brittle. Hard to break.	glasslike white center
0314B	81.3	1.3	17.4	--	--	--	--	7.0	NA	NA/2 days	Brittle. Hard to break.	glasslike white center
0323A	81.3	1.3	17.4	--	--	--	--	7.0	10.43	1 day/2 days	Hard brittle. Will not crumble.	glasslike white center
0322B	61.9	9.72	28.4	--	--	--	--	25.5	10.14	NA/2 days	Crumbles under very light pressure.	white limestone

NA = Not measured or not applicable
SS = Sodium silicate

C-1

BASIC INFORMATION ON LABORATORY PREPARATION OF SODIUM SILICATE - LEAD NITRATE FORMULAS

	CHEMICAL INGREDIENTS (P.B.W.)							% Pb			FINAL	MATERIAL
MIX NO.	H₂O	CaCl2	SS	Pb(NO3)2	LIME	P.C.	OTHER	SOLIDS	pH	GEL/DRY TIME	CONSISTENCY	APPEARANCE
0322A	64.8	7.0	24.2	4.0	--	--	--	7.11	10.81	NA/1 day	Falls apart on handling.	white powder
0324A	64.8	7.0	24.2	4.0	--	--	--	7.11	9.51	NA/1 day	Falls apart on handling.	white powder
0412A	80.0	.72	12.0	7.2	--	--	--	22.6	10.48	2 hrs/1 day	Crumbles under heavy pressure.	limestone
0413A	80.0	.38	12.0	7.2	--	--	--	22.9	10.51	2 hrs/1 day	Crumbles under heavy pressure.	limestone

NOTE: All water in recipe shown in H₂O column
Chart in increasing order of Pb content
P.B.W. = Parts by Weight
Celite = diatomaceous earth
P.C. = Portland Cement
SS = Sodium Silicate
NA = not measured or not applicable

BASIC INFORMATION ON LABORATORY PREPARATION OF
SODIUM SILICATE - LEAD NITRATE FORMULAS

	CHEMICAL INGREDIENTS (P.B.W.)							% Pb SOLIDS	pH	GEL/DRY TIME	FINAL CONSISTENCY	MATERIAL APPEARANCE
MIX NO.	H_2O	CaCl2	SS	Pb(NO3)2	LIME	P.C.	OTHER					
0323B	81.3	1.11	17.4	0.196	--	--	--	0.65	10.43	NA/2 days	Fused mass hard to break.	glasslike white center
0412B	81.3	--	17.4	0.196	--	--	CaCO3 1.11	0.65	NA	2 hrs/1 day	Fused mass hard to break.	glasslike white center
0412C	80.2	--	19.6	0.22	--	--	--	0.89	11.31	liquid/in sealed jar	Oven dried sample very hard.	glasslike clear center
0330A	76.5	--	0.396	0.48	--	--	Calite 22.62	1.27	10.51	1 day/2 days	Crumbles under moderate pressure.	Claylike Homogeneous
0305B	55.8	.45	4.52	1.0	12.75	2.55	--	1.41	NA	1 hr/less than day	Crumbles under slight pressure.	Caked dirt
0406A	78.6	2.81	7.25	0.435	--	--	HNO3 PbOH	2.59	8.01	NA/2 days	Crumbles under moderate pressure.	Limestone
0414A	82.0	1.4	16.28	0.81	--	--	--	2.74	NA	2 hr/1 day	Brittle and hard to break.	glasslike white center
0308B	55.4	0.34	4.52	1.94	12.6	25.2	--	2.72	NA	2 hr/1 day	Crumbles under slight pressure.	Caked dirt
0314E	79.0	--	20.0	1.0	--	--	--	2.97	NA	NA/NA	Liquid.	Liquid/discarded
0315D	80.0	1.0	18.0	1.0	--	--	--	3.13	NA	NA/24 hrs	Crumbles under moderate pressure.	glasslike white center
0316A	71.5	--	17.8	1.8	8.9	--	--	3.94	NA	1 hr/24 hrs	Crumbles under moderate pressure.	Limestone

NOTE: All water in recipe shown in H_2O column
Chart in increasing order of Pb content
P.B.W. = Parts by Weight
Calite = diatomaceous earth
P.C. = Portland Cement
SS = Sodium Silicate
NA = not measured or not applicable

C-3

END

FILMED

10-84

DTIC